

April 5, 2021

Mr. Ricky Vargas
Project Manager
Land and Redevelopment Programs Branch
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United States Environmental Protection Agency, Region 2
290 Broadway, 25th Floor
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**Re: No Further Investigation Justification for Catalyst Beads
Response to USEPA Comment Letter, dated September 22, 2020
Former Chevron Perth Amboy Facility
Perth Amboy, New Jersey
SRP PI # 003621
EPA ID No. NJD081982902**

Dear Mr. Vargas,

INTRODUCTION

The United State Environmental Protection Agency (USEPA) and New Jersey Department of Environmental Protection (NJDEP) provided a comment letter dated September 22, 2020 in response to Chevron's Catalyst Beads document dated March 24, 2020. This document was submitted for the former Chevron Perth Amboy Facility at 1200 State Street, Perth Amboy New Jersey (Facility). The specific comments provided by the Agencies are as follows:

1. Closing Section, Page 5, requests a NFA determination for PCBs at the former Chevron Perth Amboy Facility. We cannot evaluate PCBs with the information provided. The Catalyst Beads letter could request a "NFI Justification for Catalyst Beads", provided all the information required to make such determination is submitted.
2. Page 4, Conclusions states, "Catalyst beads used in the refining of crude oil at the Facility were initially made of naturally occurring aluminosilicate (i.e., Fuller's Earth). Later, with the advances in catalytic cracking technology, the catalyst beads consisted of synthetic aluminosilicates and zeolites coated with nickel, vanadium, platinum, palladium, rhenium, and other noble metals. PCBs were not used in the refining processes performed at the Facility and are not considered to be a potential contaminant in fill material." Please submit the information Chevron used to determine what the Catalyst Beads used at the former Chevron Perth Amboy facility consisted of or Catalyst Beads area(s) soil boring analytical data to corroborate Chevron's conclusion.

In response to the USEPA comments, Chevron is providing additional information on the composition of catalyst beads used at the Former Chevron Perth Amboy Facility. As Chevron presented previously and as noted in Comment #2, above, historically catalysts used in the refining of crude oil into various petroleum products were comprised of naturally occurring aluminosilicates (clays). With technological advances in the petroleum industry, synthetic aluminosilicates and zeolites were developed. The manufactured zeolite catalysts were impregnated with various metals (nickel, vanadium, platinum, palladium, rhenium for example) to increase their cracking activity and function.

Documents reviewed to determine the composition of catalyst beads used for the petroleum industry are attached. The former Chevron Perth Amboy Facility was a full-service refinery that produced gasoline, fuel oil, and asphalt. Research reflects that the catalysts used for the refining of crude oil into the products listed above consisted of an aluminosilicate carrier impregnated with various metals (nickel, vanadium, platinum, palladium, rhenium) depending on the feedstock and end product. Based on this information, aluminosilicate catalyst beads used in the refining processes performed at the former Chevron Perth Amboy Facility were not impregnated with PCBs. Chevron technical experts were consulted regarding the potential use of PCBs in the refining processes performed at the Former Chevron Perth Amboy Facility. Chevron's technical experts explained that it was not standard practice to use PCBs or PCB oil to prepare aluminosilicate catalyst beads for use in the petroleum refining process, and they could not confirm that PCBs were used in past catalyst bead formulations.

In previous comment letters from USEPA and NJDEP, the following has been stated: "the Department is well acquainted with another refinery that as part of pilot study to enhance the refining/cracking process, impregnated catalyst beads made of aluminosilicate material (ASM) with polychlorinated biphenyls (PCBs, specifically Aroclor 1254)." Review of available literature (see select documents Attached) indicates aluminosilicate catalysts have been widely used in the petroleum refining industry since the 1930s. These aluminosilicate catalysts were impregnated with various metals (i.e. nickel, vanadium, platinum, palladium, rhenium) to enhance the cracking/refining process. However, in the available literature there is no mention of impregnating aluminosilicate catalyst beads with PCBs as a standard industry practice to enhance the refining/cracking process. The Department stated that the impregnation of catalyst beads with PCBs was performed as part of a pilot study at a specific facility, indicating that this process was likely part of a research and development program, and was not a standard practice in the petroleum refining industry.

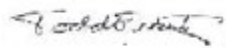
As previously stated in Chevron's March 24, 2020 Catalyst Bead document, Chevron did not perform any research and development activities at the former Chevron Perth Amboy Facility. The refining processes employed at the former Chevron Perth Amboy Facility followed standard petroleum industry processes using aluminosilicate catalysts impregnated with various metals, which would not have involved the introduction of PCBs or PCB oils.

CLOSING

Based on the information presented herein, investigation of PCBs associated with the spent catalyst beads identified in fill material at the former Chevron Perth Amboy Facility is not warranted. Chevron requests approval by USEPA and NJDEP of this No Further Investigation Justification for catalyst beads at the former Chevron Perth Amboy Facility.

Should you require any additional information, please contact me directly at (732) 738-2226.

Sincerely,



Todd Frantz
Senior Project Manager
Parsons

cc: Mr. Brian Connors, CEMC
Mr. Charlie Zielinski, NJDEP
Mr. Brendan Leehan, Buckeye Perth Amboy Terminal, LLC
Ms. Krista Manley, Buckeye Perth Amboy Terminal, LLC

ATTACHMENTS

Bricker, Maureen et. al., Hydrocracking in Petroleum Processing, Handbook of Petroleum Processing, Springer International Publishing Switzerland, 2014.

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Arndt, John H. (Berkeley, CA), Jacobson, Robert L. (Vallejo, CA), 1993. Platinum-rhenium Catalyst, Chevron Research and Technology Company (San Francisco, CA), United States Patent No. 5198404. <https://www.freepatentsonline.com/5198404.html>

No Further Investigation Justification for Catalyst Beads
Response to USEPA Comment Letter, dated September 22, 2020
Former Chevron Perth Amboy Facility
April 5, 2021

bcc: Scott Nelson, Brown and Caldwell
Todd Reinold, TRC

Doc ID: 2021-004-37

Hydrocracking in Petroleum Processing

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Abstract

Hydrocracking is a flexible catalytic refining process that can upgrade a large variety of petroleum fractions. Hydrocracking is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils, including residue. The process adds hydrogen which improves the hydrogen to carbon ratio of the net reactor effluent, removes impurities like sulfur to produce a product that meets the environmental specifications, and converts the heavy feed to a desired boiling range. The chemistry involves the conversion of heavy molecular weight compounds to lower molecular weight compounds through carbon-carbon bond breaking and hydrogen addition. The main products have lower boiling points, are highly saturated, and generally range from heavy diesel to light naphtha. Hydrocracking processes are designed for, and run at, a variety of conditions. The process design will depend on many factors such as feed type, desired cycle length, and the desired product slate. Hydrocracking is a process that is suitable to produce products that meet or exceed all of the present environmental regulations. Hydrocracking reactions proceed through a bifunctional mechanism. Two distinct types of catalytic sites are required to catalyze the steps in the reaction sequence. The cracking and isomerization reactions take place on the acidic support. The acid can be an amorphous silica alumina or a zeolite. The metals provide the hydrogenation function. The metals are typically noble metal (palladium, platinum) or non-noble metal sulfides from group VIA (molybdenum, tungsten) and group VIIA (cobalt, nickel).

Catalyst manufacturing can be done by a variety of methods. The method chosen represents a balance between the manufacturing cost and the degree to which the desired chemical and physical properties are achieved. Many companies are involved in the licensing of the process and the production of a variety of hydrocracking catalysts.

Keywords

Hydrocracking; Hydroprocessing; zeolite; Y zeolite; Beta zeolite; Ni, W; Pt base metals; Base metal sulfide; Noble metal; Single stage; Two stage; Vacuum gas oil (VGO); Unconverted oil (UCO); Diesel; Distillate; Gasoline; Cracking; Isomerization; Hydrogenation; Aromatic saturation; Hydrodesulfurization HDS; Hydrodenitrogenation HDN; Catalyst manufacture; Cetane number; Smoke point; Cold flow properties

Introduction

Hydrocracking is a flexible catalytic refining process that can upgrade a large variety of petroleum fractions. Hydrocracking is commonly applied to upgrade the heavier fractions obtained from the

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distillation of crude oils, including residue. Tables 1 and 3 show the feedstock used in hydrocracking as well as the products obtained (Scherzer and Gruia 1996; Robinson and Dolbear 2006). The process adds hydrogen which improves the hydrogen to carbon ratio of the net reactor effluent, removes impurities like sulfur to produce a product that meets the environmental specifications, and converts the heavy feed to a desired boiling range. The chemistry involves the conversion of heavy molecular weight compounds to lower molecular weight compounds through carbon-carbon bond breaking and hydrogen addition. The main products have lower boiling points, are highly saturated, and generally range from heavy diesel to light naphtha. Hydrocracking processes are designed for, and run at, a variety of conditions. The process design will depend on many factors such as feed type, desired cycle length, and the desired product slate. However, units generally operate at the following conditions: liquid hourly space velocity (LHSV), 0.5–2.0; H₂ circulation, 5,000–10,000 SCFB (standard cubic feet per barrel); H₂ partial pressure, 1,500–2,000 psia (103–138 bars); and start of run (SOR) temperatures, from 650 °F (288 °C) to 725 °F (385 °C). Hydrocracking is a process that is suitable to produce products that meet or exceed all of the present environmental regulations.

The demand for hydrocracking is predicted to be a stable growth market for the foreseeable future Table 3. The installed hydrocracking capacity is estimated to be between six and seven million barrels per stream day (bpsd). The estimate of current installed catalyst capacity in the world is 30,000 MT. The 2013 OPEC World Oil Outlook Table 3 shows that the demand for hydrocracking increases with a continuing value of distillate products over gasoline products as well as a large increasing demand for desulfurization processes which reflects the lower sulfur requirements in gasoline and diesel around the world. With the changing market and the change in fuel consumption causing the shift from high gasoline demand to high distillate demand, many refiners are conducting modifications to their existing facilities to allow an improved integration of their refinery or another change in the configuration to allow flexible product needs. Since 2009, the worldwide capacity for hydrocracking has grown about 2 %, the global demand for diesel has grown about 2 %, and over the next 3 years, the demand for combined hydrotreating and hydrocracking is projected to grow by 6 % per year (http://www.opec.org/opec_web/static_files_project/media/downloads/publications/WOO_2013.pdf).

Brief History

Modern hydrocracking technology has been in use since 1960. However, there is a long history of hydrocracking that began early in the twentieth century (Scherzer and Gruia 1996; Robinson and Dolbear 2006). Hydrocracking technology was developed in Germany in the 1910s when it was used for coal conversion to secure a supply of liquid fuels from domestic coal deposits. The first plant for the hydrogenation of brown coal began in Germany in 1927. Coal conversion to liquids was a high pressure, 3,000–10,000 psig (207–690 bar) and high-temperature (700–1,000 °F, 371–538 °C) catalytic process (Ministry of Fuels and Power 1947). From 1925 to 1930, I.G. Farbenindustrie in Germany in collaboration with Standard Oil of New Jersey developed hydrocracking technology to convert heavy gas oils to lighter fuels (Heinemann 1981). Other groups did research work to develop technology to upgrade heavier petroleum fractions (Pier 1949). After World War II, the Middle Eastern crudes became available, and their gas oils and cracked stocks were easily processed in FCC. So hydrocracking became less important. Catalytic cracking processes proved to be more economical for converting heavy petroleum fraction to gasoline based on the demands for gasoline and environmental regulations of that time.

Table 1 Hydrocracking feeds and products from the processing

Feedstock	Products
Straight-run gas oils	LPG
Vacuum gas oils	Motor gasoline
FCC cycle oils and decant oils	Reformer feeds
Coker gas oils	Jet fuels
Thermally cracked stocks	Diesel fuels
Deasphalted oils	Heating oils
Straight-run and cracked naphtha	Olefin plant feedstocks, lube oils, lube plant feedstock, FCC feedstock
Fischer-Tropsch liquids	Distillate fuels
Tar sands	Distillate fuels

Table 2 2013 OPEC World Oil Outlook

Global capacity requirements by process, 2012–2035 mb/day				
	Additional requirements		Total additions	
	To 2018	To 2020	2020–2030	To 2035
Existing projects				
Hydrocracking	2.2	1	3.2	6.4
Desulfurization	6.9	6.6	13.5	26.9
Vacuum gas oil/resid	0.9	0.7	1.7	3.3
Distillate	2.8	5	9.8	17.5
Gasoline	3.2	1	2	6.1

Table 3 Types of hydrocracking processes

Unit type	Typical conversion	Total pressure, bar/psig	Hydrogen partial pressure, bar/psig	Reactor temperature, °C/°F
Mild (MHC)	20–40	60–100/870–1,450	20–55/290–840	350–440/662–824
Moderate/medium pressure	40–70	100–110/ 1,450–1,600	50–95/725–1,380	340–435/644–815
Conventional	50–100	110–200/ 1600–2,900	95–140/1,390–2,030	340–435/662–842
Resid hydrocracking (LC-fining)	65–100	97–340/ 1,400–3,500	73–255/1,050–2,625	385–450/725–914
Slurry hydrocracking	80–97	138–241/ 2,000–3,500	103–206/1,500–3,000	426–471/800–880

Hydrocracking technology reemerged in the 1950s with the growth of the transportation industries. In the mid-1950s, the automotive industry began to make high-performance cars with engines that required high-octane gasoline. This need caused a large expansion of the catalytic cracking industry to produce gasoline. But the by-products were large quantities of refractory cycle oils that were difficult to convert to gasoline and lighter products. Hydrocracking was able to convert these difficult by-products to desirable gasoline and diesel fractions and so was adopted in some refineries. Simultaneously, railroads switched from steam to diesel engines, and commercial aviation, using more jet fuel, began to emerge as a large industry. All three of these industries increased the demand

for refined petroleum products. The flexibility of the newly developed hydrocracking processes allowed the production of fuels from heavier feedstocks.

In early 1960, Chevron Research Co. announced a new hydrocracking process called “Isocracking” (Stormont 1959). Unocal, then known as Union Oil Co., in collaboration with ESSO, introduced the hydrocracking process called “Unicracking-JHC” (Oil Gas J 1960). In the late 1950s, UOP announced the “Lomax” hydrocracking process (Sterba and Watkins 1960). By the mid-1960s, seven different hydrocracking processes were offered for license (Scott and Patterson 1967).

Presently, various environmental regulations stipulate a low level of sulfur and in some cases a low level of aromatics in both gasoline and diesel products; this has spurred a growth in a variety of hydroprocessing complexes around the world. In the United States, the Tier 2 gasoline sulfur program reduced the sulfur content of gasoline by up to 90 % from an uncontrolled level. An average sulfur level 30 ppm was phased in from 2004 to 2007. The final Tier 3 gasoline sulfur program lowers the sulfur level to 10 ppm. This level is planned but it has not yet been mandated (<http://www.epa.gov/otaq/standards/fuels/gas-sulfur.htm>). However, in Europe an essentially zero sulfur level is the specification, and in Japan, they are moving toward the 10 ppm S specification (http://transportpolicy.net/index.php?title=EU:_Fuels:_Diesel_and_Gasoline#Technical_Standards; http://transportpolicy.net/index.php?title=Japan:_Fuels:_Diesel_and_Gasoline). As the sulfur level required in gasoline and diesel reached low levels, a large growth in both hydrotreating and hydrocracking capacity grew in the world and is expected to continue to grow over the next decade (<http://www.hydrocarbonpublishing.com>). Even when a refiner in a certain area of the world does not need the stringent specification for their region, the process is designed for the stiffer requirement so that the refiners are able to export their products to any area of the world to improve their economics. Limitations have also been put on the sulfur levels that diesel may contain. As shown in Fig 1, the level of sulfur in diesel is low in North America, Europe, Australia, and Japan and higher in other areas of the world (Akumu 2012).

Refiners have begun to use heavier sources of crudes to increase their margin on the refined products. One of the new sources is the synthetic crudes and bitumen blends from the Canadian tar sands. This denser, hydrogen-deficient VGO needs more upgrading than hydrogen-rich feeds. Shale deposits will produce a shale oil that will need extensive upgrading to meet the product demands; arsenic is a metal that is found in shale oils that is not commonly found in other typical petroleum fractions (Wier et al.). Today, there is a shift in desired product slate. In the past there was a higher demand for gasoline, especially in the United States as the engines for automobiles were of the gasoline type. In the world, there is less demand for gasoline and more demand for distillate fuel. This change in product distribution has helped spur the demand for flexible hydrocracking processes.

The early hydrocrackers used catalysts based on iron, nickel, or nickel-tungsten metal supported on alumina or amorphous silica-alumina. Zeolite components were introduced to the catalysts during the rapid growth of hydrocracking technology during the 1960s. Zeolite-containing catalysts were significantly different than amorphous catalysts; zeolites had higher activity and gasoline selectivity and better ammonia tolerance (Baral and Huffman 1971; Bolton 1976). In the United States, hydrocracking was primarily used in the production of high-octane gasoline, but in the other parts of the world, it was used primarily for the production of middle distillates. Different catalyst formulations are selected depending on the product slate desired by the refiner.

Flow Schemes

Hydrocracking units can be configured in a number of ways. The unit can consist of one or two reactors with either one or multiple catalysts. The process can use one or two stages and be operated in once-through or recycle mode. The choice of the configuration depends on the feed properties and the specific product slate desired by the refiner. The five main types of operating units are mild, moderate/medium pressure, conventional, partial conversion, and resid hydrocracking. These are shown in Table 3.

Once-Through Configuration

Figures 1–3 show a schematic of a once-through hydrocracking unit, which is the simplest configuration for a unit. This configuration is a variation of the single-stage hydrocracking unit with recycle configuration. The feed mixes with hydrogen and goes to the reactor. The net reactor effluent goes to fractionation, with the unconverted oil being removed as the heaviest cut from the bottom of a fractionation column. This type of unit is the lowest cost hydrocracking unit and can process heavy, high-boiling feedstocks and produce high-value products including unconverted materials which become feedstock for FCC units, ethylene plant, or lube oil units. In general, the conversion of the feedstock to products is 30–80 vol.%, but a range as high as 90 vol.% is possible with some feeds.

Single Stage with Recycle Hydrocracking

The most widely found hydrocracking unit is the single-stage configuration in which the recycled oil is sent back to the reactor section to maximize conversion at a reduced conversion per pass. Figure 3 depicts this type of unit. It is the most cost-effective design for 100 % conversion and is especially used to maximize the heaviest product cut such as diesel or jet fraction.

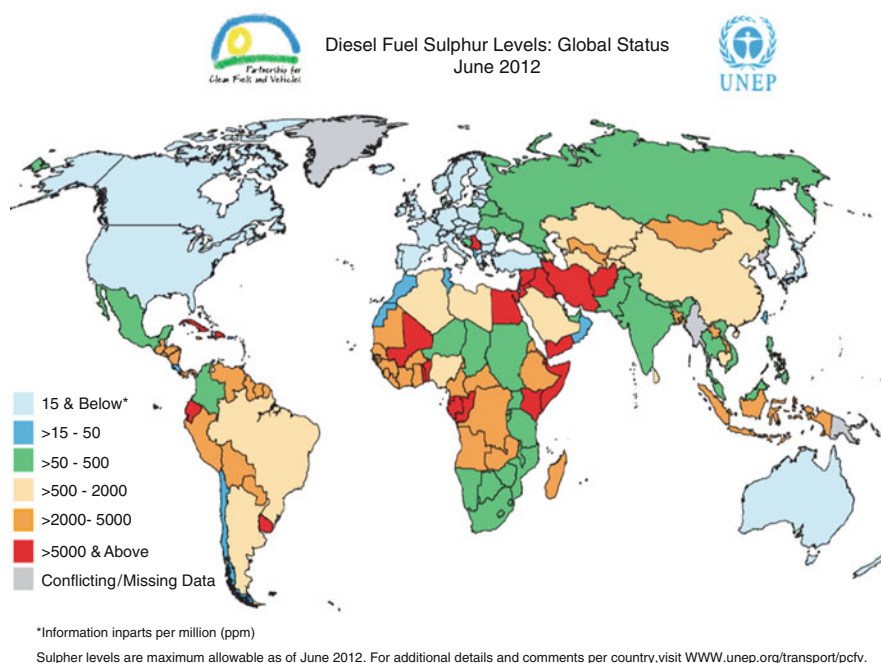


Fig. 1 Global levels of sulfur in diesel fuel

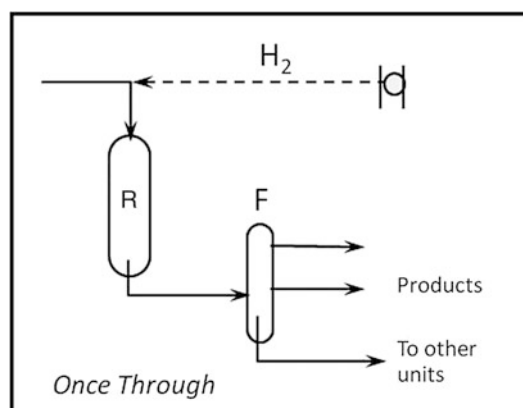


Fig. 2 Once-through hydrocracking unit

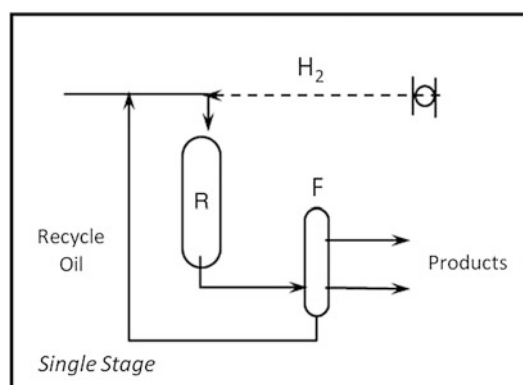


Fig. 3 Single-stage hydrocracking unit with recycle

A more detailed flow diagram of the reactor section in a single-stage hydrocracking unit (than those shown in either Figs. 2 or 3) is shown in Fig. 4. The fresh feed is preheated to reaction temperature by passing it through heat exchangers and a heater and then passed downward through the catalyst bed in the presence of hydrogen. The effluent from the reactors goes through a series of separators where hydrogen is recovered and, together with makeup hydrogen, is recycled to the reactors. The liquid product is sent to fractionation where the final products are separated from the recycled oil and any unconverted oil. In once-through units, the unconverted oil is sent out of the unit, as previously described. In units designed to operate with recycle, the recycle oil combines with the fresh feed, as shown in Fig. 4.

As described in the Chemistry section (section “[Chemistry](#)”), the reaction section fulfills two functions: hydrotreating and hydrocracking. This is shown in Fig. 4 as separate reactors, though both functions can be achieved in a single reactor when using some types of catalysts, e.g., an amorphous catalyst. In most modern configurations, different catalysts are used for the hydrotreating and the hydrocracking sections; however, if both types of catalyst can be loaded in the same reactor, separate vessels are not needed. When using both pretreatment and cracking configurations, the first catalyst (a hydrotreating catalyst) converts organic sulfur and nitrogen from hetero-compounds in the feedstock to hydrogen sulfide and ammonia, respectively. The deleterious effect of gas-phase H_2S and NH_3 on hydrocracking catalysts is considerably less than that of the corresponding organic hetero-compounds in the liquid phase. The hydrotreating catalyst also facilitates the hydrogenation

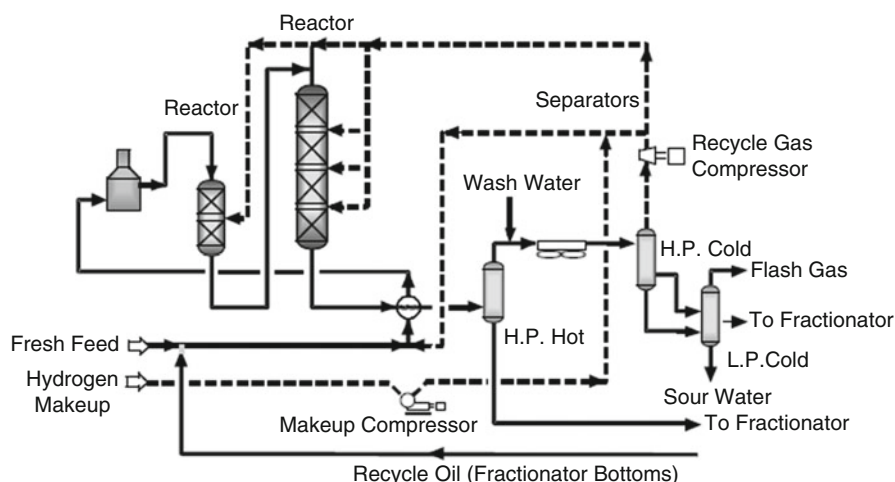


Fig. 4 Typical flow diagram of reactor section of single-stage hydrocracking unit

of aromatics. In the single-stage configuration, the products from the hydrotreating reaction zone are passed over a hydrocracking catalyst where most of the hydrocracking takes place. The conversion occurs in the presence of NH_3 , H_2S , and small amounts of unconverted amounts of hetero-compounds. The hydrotreating catalyst is designed to convert the hetero-compounds in the feed-stock. Typically, such catalysts comprise sulfided molybdenum and nickel on an alumina support. The reactor operates at temperatures varying from 570 to 800 °F (300–425 °C) and hydrogen pressures between 1,250 and 2,500 psig (85–170 bar). Under these conditions, heteroatom elimination, significant hydrogenation, and some cracking also take place. The cracking catalyst operates at the same hydrogen pressures but at temperatures varying from 570 to as high as 840 °F (300–450 °C) for amorphous hydrocracking catalysts and up to 440 °C (825 °F) for zeolite-containing catalysts.

The effluent from the reactor is passed through high- and low-pressure separators, where hydrogen is recovered. The separated hydrogen combined with fresh hydrogen is recycled to the reactor. The liquid product is sent to fractionation where the final products are separated from the recycled oil and any unconverted oil. Fractionation produces the light ends (C_4^-) and liquid products. The liquid products are fractionated into the various product streams. Table 4 shows the product fractions and the application of the product.

Two-Stage Recycle Hydrocracking

The two-stage hydrocracking process configuration is also widely used, especially for high-capacity units. In two-stage units, the hydrotreating and some cracking take place in the first stage. The effluent from the first stage is separated and fractionated, with the unconverted oil passing to the second stage for further reaction. The reactor effluent from the second-stage reaction section goes back to the common fractionator. A simplified schematic of a two-stage hydrocracker is shown in Fig. 5. The catalysts in the first stage are the same types as those used in the single-stage configuration. The reaction environment in the second stage may contain ammonia or hydrogen sulfide depending on the unit design. If the recycle gas is scrubbed to low hydrogen sulfide levels, the environment in the second stage is considered “sweet”; if not then the second stage is “sour.” The catalyst in the second stage may be operating in the near absence of ammonia and hydrogen sulfide. Thus the catalysts used in the second stage need to be tailored for that reaction environment to maximize desired product selectivity.

Table 4 Product fractions and application of the product from the hydrocracking process

Fraction	Product	Use
Light gases, C ₃ , C ₄	C ₃ , C ₄	Fuel gas, feed for alkylation, recovered as LPG, petrochemical feedstock
Light naphtha	C ₅ -80 °C/C ₅ -175 °F	Gasoline pool component, feed to isomerization unit
Heavy naphtha	80–150 °C/175–300 °F	Reformer feedstock to be converted in high-octane gasoline and hydrogen or aromatics for petrochemicals
Jet fuel/kerosene	150–290 °C/300–550 °F	Fuel for turbine engines
Diesel fuel	290–370 °C/550–700 °F	Fuel for diesel engines
Unconverted oil	700 °F ⁺	Recycle feed or feedstock for lube plants or ethylene plants or FCC plants

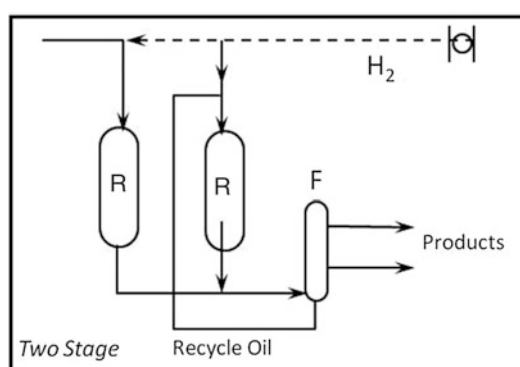


Fig. 5 Two-stage hydrocracking

Separate Hydrotreating with Two-Stage Hydrocracking

A variation of the typical two-stage hydrocracking process occurs when the first stage does not contain hydrocracking catalyst in the first stage. Separate hydrotreating scheme uses common or separate hydrogen circulation loop. Figure 6 shows the flow scheme in which each stage has a separate hydrogen circulation loop, allowing for operation of the second stage in the near absence of hydrogen sulfide and ammonia.

Design and Operation of Hydrocracking Reactors

Hydrocracking reactors are run as downflow, fixed-bed catalytic reactors, generally operating in trickle-flow regime. The reactors are vessels with thick wall constructed from special materials due to the severity of the conditions during hydrocracking, high pressure and temperature, and the presence of hydrogen, ammonia, and hydrogen sulfide. The reactors are usually cylindrical vessels fabricated from 2 ¼ Cr-1 Mo or 3 Cr-1 Mo material with stabilized austenitic stainless steel weld overlay or liner, for added corrosion protection. More specialized materials, in which a small amount of vanadium is added to the 2 ¼ Cr-1 Mo or 3 Cr-1 Mo reactor base metal to increase its strength characteristics, have also been used. A typical drawing of a hydrocracking reactor is shown in Fig. 7.

The size of the hydrocracking reactors varies widely depending on the design conditions and is dependent on the desired mass flux for good flow distribution and acceptable pressure drops.

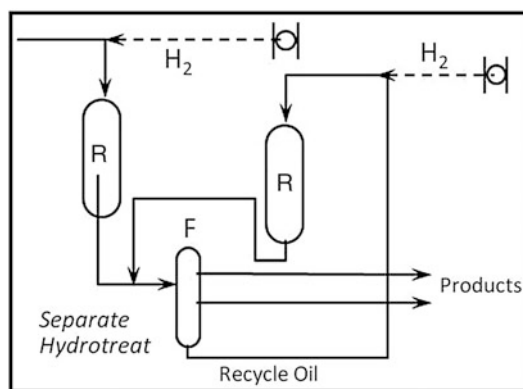


Fig. 6 Separate hydrotreating with two-stage hydrocracking

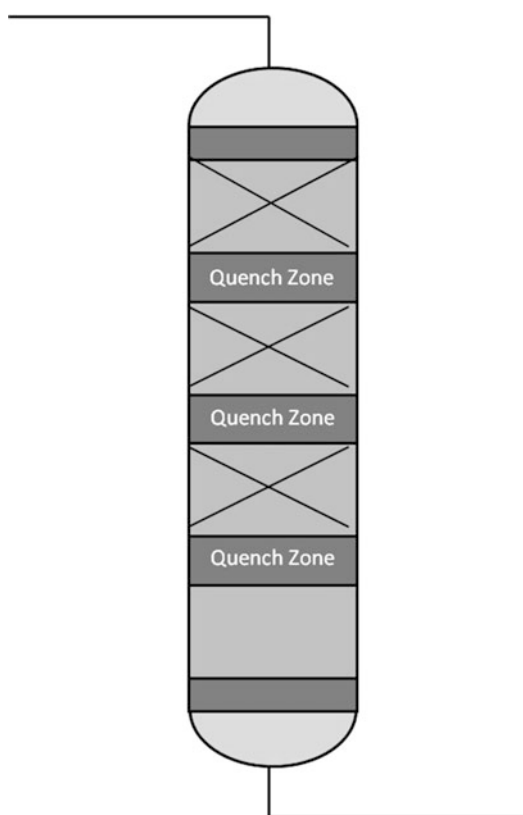


Fig. 7 Typical hydrocracking reactor

Commercially, reactors with inside diameters of up to 20 ft (6.096 m) have been fabricated. Depending on the design pressure and inside diameter, the thickness of the reactor walls can be as much as 1 ft (30 cm). Since hydrotreating/hydrocracking reactions are exothermic, heat release is a common feature for all hydrocrackers; thus reactor temperature control has to be exercised. As shown schematically in Fig. 7, a hydrocracking reactor will contain several separate catalyst beds in order to manage heat release with quench in between the beds. The number of catalytic beds in a reactor and their respective lengths are determined for temperature rise profile and flow distribution. The maximum acceptable temperature rise per bed depends on the type of catalyst and operational

safety criterion. The heat release is function of feed type, operating severity, and catalyst type. The maximum temperature that determines the end of run depends on the reactor metallurgy and design. A typical reactor operated to maximize conversion to naphtha will have as many as five or six beds. A typical reactor operated to produce middle distillate will have three or four beds. Commercial catalyst beds can be as deep as 30 ft (10 m). A typical hydrotreating reactor will have two or three beds if the feed is straight-run material and up to five beds if the feed contains appreciable amounts of cracked or aromatic material.

Since hydrocracking is an exothermic process, the fluids exiting one catalyst bed have to be cooled prior to entering the next catalyst bed in order to control reaction rate and allow a safe and stable operation. This is accomplished by injecting cool hydrogen for quench. Cold hydrogen gas, introduced in the quench zones, is used to control reactor temperature and improve hydrogen partial pressure. The quench zones which separate successive catalyst beds have the following functions:

- To cool the partially reacted fluids with hydrogen quench gas
- To assure a uniform temperature distribution of the fluids entering the next catalyst bed
- To mix efficiently and disperse evenly the fluids over the top of the next catalyst bed

Furthermore, the temperature distribution in the cooled fluids entering the next catalyst bed has to be uniform in order to minimize the radial temperature gradients in successive catalyst beds. Unbalanced temperatures in a catalyst bed could result in different reaction rates in the same bed. This can lead to different deactivation rates of the catalyst and, in worse cases, to temperature excursions.

It is also important to achieve a good mass flow distribution. The effective vapor/liquid mixing and uniform distribution of fluids over the top of the catalyst bed, accomplished in the quench zone, reestablishes an even mass flow distribution through the catalyst bed. Another important parameter is liquid flux (lb/h/ft^2 of cross-sectional area). While gas mass flux has practically no influence on liquid distribution, liquid mass flux is determinant in avoiding poor distribution in the catalyst bed. Operation at a liquid mass flux of more than $2,000 \text{ lb/h/ft}^2$ is recommended; operation at liquid fluxes lower than $1,500 \text{ lb/h/ft}^2$ is discouraged. Furthermore, if the liquid mass flux is below the recommended limit, increasing the gas mass flux may not improve the liquid distribution.

Hydrocracking Reactor Operation

During operation, the hydrocracking catalyst gradually loses its activity. In order to maintain constant conversion of feedstock to products, the average bed temperature is gradually increased. The temperature increase in many cases is very small, less than 2°F/month (1°C/month). When the average bed temperature reaches a value close to the design maximum, the catalyst has to be replaced or reactivated. Because the required temperature increase per unit time is relatively small, the reactor can be operated with the same catalyst for several years before replacement of the deactivated catalyst becomes necessary. Similar changes take place in the pretreating reactor.

The rates of reaction determine the key properties of a hydrocracking catalyst: initial activity, selectivity, stability, and product quality. The temperature required to obtain the desired product at the start of the run measures the initial activity. In general, the catalyst activity is a measure of the relative rate of feedstock conversion. In hydrocracking, activity is defined as the required temperature obtaining a fixed conversion under certain process conditions. Hydrocracking conversion is usually defined in terms of shifting molecules above a specified true boiling point (TBP) to products boiling below the same TBP, commonly referred to as a cut point:

Table 5 Chemical basis for product quality measurements

Desired product quality	Chemical basis
High smoke point	Low concentration of aromatics
Low pour point	Low concentration of <i>n</i> -paraffin
Low freeze point	Low concentration of <i>n</i> -paraffin
Low cloud point	Low concentration of <i>n</i> -paraffin
Low CFPP (cold flow pour point)	Low concentration of <i>n</i> -paraffin
High octane	High ratio of <i>i</i> -/ <i>n</i> -paraffin
	High concentration of aromatics
Cetane number	Measure of hydrocarbon type
Cetane index	Estimate of cetane number based on distillation range and density

$\% \text{Net Conversion} = ((EP^+_{\text{feed}} - EP^+_{\text{product}}) / EP^+_{\text{feed}}) \times 100$ where EP^+ indicates the fraction of material in the feed or product boiling above the desired cut point.

Catalyst selectivity is a measure of the rate of formation of a desired product relative to the rate of conversion of the feed (or formation of other products). Hydrocracking selectivity is expressed as the yield of desired product at a specific conversion. Yield is determined by the rate of formation of the desired product relative to the feed rate. At 100 % conversion, catalyst yield equals catalyst selectivity. Hydrocracking selectivity is affected by operating conditions. In general, more severe operating conditions cause higher selectivity to secondary products.

Catalyst stability is a measure of change of reaction rate over time. Hydrocrackers are typically operated in the constant conversion mode, with temperature adjustments made to maintain the desired conversion. Hydrocracking activity stability is defined as the temperature change per time required for maintaining constant conversion. Changes in product yield over time also occur. Hydrocracking yield stability is defined as the yield change with time at constant conversion and is usually expressed as a function of temperature.

The product quality is a measure of the ability of the process to yield products with the desired use specification such as pour point, smoke point, or octane. Table 5 shows some of the important product quality measurements and the chemical basis for these measurements.

Chemistry

The chemistry of hydrotreating and hydrocracking is commonly taken together and termed hydroprocessing and is similar for both sections of the hydroprocessing unit. There is not a clear distinction between the hydrotreating and hydrocracking chemistries because there is some hydrocracking that occurs in the hydrotreating reactor especially when high temperatures are used, either at the end of the cycle or when low sulfur in the product is the target. Hydrotreating converts the S heteroatom in organic sulfur-containing compounds to H_2S , the N heteroatom in nitrogen-containing compounds is converted to NH_3 , and if present the O heteroatom in oxygen-containing compounds is converted into H_2O . Hydrocracking converts the higher carbon number feed molecules to lower molecular weight products by cracking the side chains and by saturating the aromatics and olefins. Hydrocracking catalysts will also remove any residual sulfur and nitrogen which remain after the hydrotreating, usually in the heavy molecular weight compounds. Table 6 is a list of the hydroprocessing reactions. The evolution of

Table 6 List of the hydroprocessing reactions

Reaction type	Reaction
Minimal C–C bond breaking	
Hydrodesulfurization (HDS)	$R-S-R^* + 2H_2 \rightarrow RH + R^*H + H_2S$
Hydrodenitrogenation (HDN)	$R=N-R^* + 3H_2 \rightarrow RH + R^*H + NH_3$
Hydrodeoxygenation (HDO)	$R-O-R^* + 2H_2 \rightarrow RH + R^*H + H_2O$
Hydrodemetallation (HDM)	$R-M + \frac{1}{2} H_2 + A \rightarrow RH + MA$
Saturation of aromatics	$C_{10}H_8 + 2H_2 \rightarrow C_{10}H_{12}$
Saturation of olefins	$R=R^* + H_2 \rightarrow HR-R^*H$
Isomerization	$n-RH \rightarrow i-RH$
Significant C–C bond breaking	
Dealkylation of aromatic rings	$\Theta-CH_2R + H_2 \rightarrow \Theta-CH_3 + HR$
Opening of naphthene rings	$Cyclo-C_6H_{12} \rightarrow C_6H_{14}$
Hydrocracking of paraffins	$R-R^* + H_2 \rightarrow RH + R^*H$
Other reactions	
Coke formation	$2 \Theta-H \rightarrow \Theta-\Theta + 2H_2$
Mercaptan formation	$R=R^* + H_2S \rightarrow HSR-R^*H$

From Springer Fundamentals of Hydrocracking

Θ aromatic, R , R^* alkyl, M Fe, Ni, or V, A metal-adsorbing material

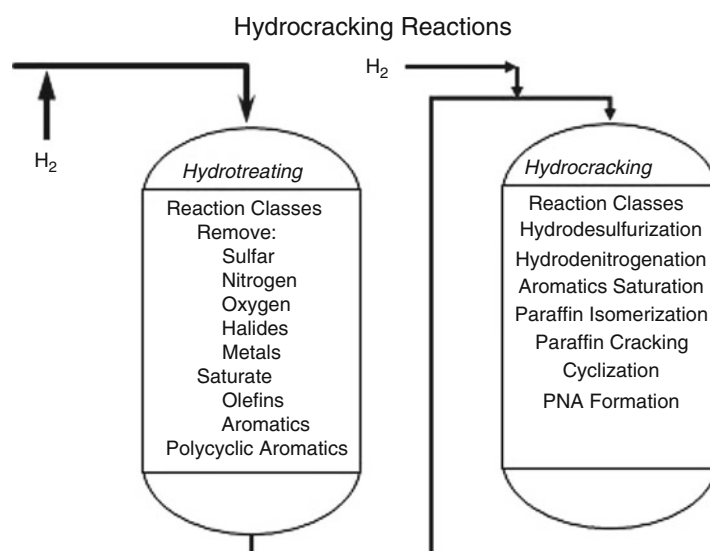


Fig. 8 Summary of hydroprocessing reaction classes in the sections of the hydrotreating and hydrocracking reactors

the reaction profile between the hydrotreating reactor and the hydrocracking reactor is shown in Figs. 8, 9, and 10.

There are two types of reactions taking place in hydroprocessing units: impurity removal (also called pretreating or hydrotreating) and cracking (also called hydrocracking). The conversions in hydroprocessing can be classified into desirable and undesirable reactions. The desirable reactions are desulfurization and denitrogenation, saturation (i.e., hydrogen addition to olefin and aromatic molecules), and cracking (i.e., reaction of side chains to reduce the molecular weight). Undesirable

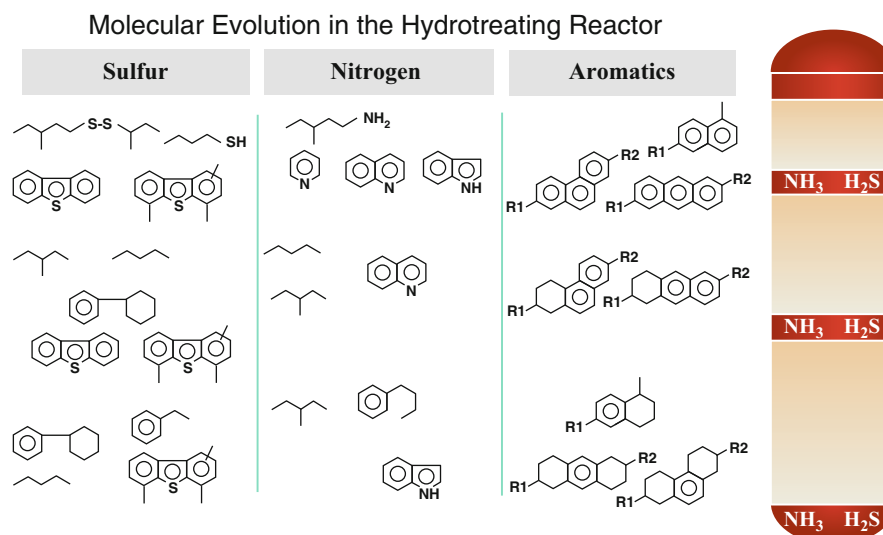


Fig. 9 Evolution of the reactions in the hydrotreating reactor

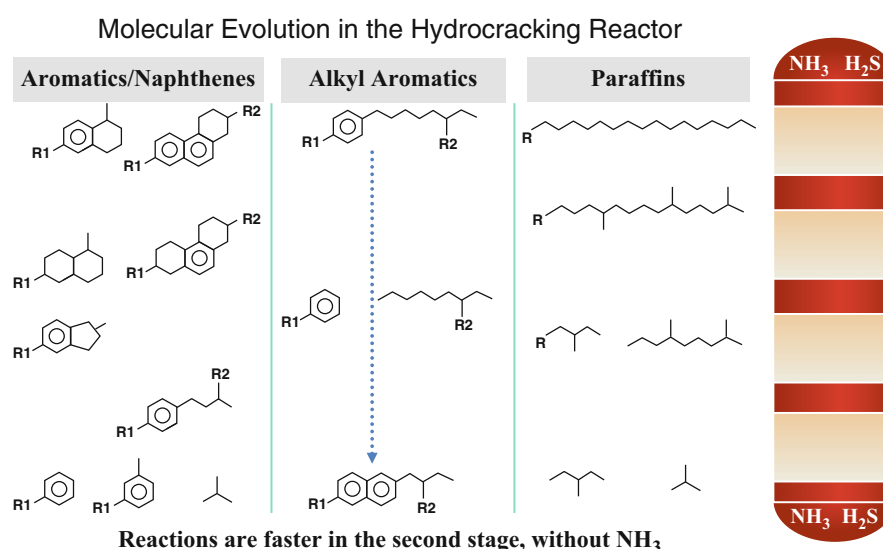


Fig. 10 Evolution of the reactions in the hydrocracking reactor

reactions are contaminant poisoning (metals deactivating the catalyst) as well as coking of the catalyst.

Hydrotreating Reactions

The hydrotreating reactions that take place are the removal of sulfur, nitrogen, organometallic compounds, oxygen, and halide. Olefin and aromatic saturation will also occur. Sulfur, nitrogen, and metals are almost always present in any type of feed, and the levels depend on the crude source and/or the conversion unit that produces an additional feedstock apart from the crude unit, such as a delayed coking unit, FCC unit, and the like. Oxygen and halides are not always present. The hydrotreating reactions proceed in the following order: metal removal, olefin saturation, sulfur

removal, nitrogen removal, oxygen removal, halide removal, and aromatic saturation. Figure 9 shows the evolution of the reactions in the hydrotreating reactor. Hydrogen is consumed in all of the treating reactions. As a guideline, the desulfurization reactions consume 100–150 SCFB/wt% S change ($17\text{--}25\text{ Nm}^3/\text{m}^3/\text{wt}\%$ change), and denitrogenation reactions consume 200–350 SCFB/wt% N change ($34\text{--}59\text{ Nm}^3/\text{m}^3/\text{wt}\%$ change). Typically the heat release in the hydrotreating section is about $0.1\text{--}0.2\text{ }^\circ\text{F}/\text{SCFB H}_2$.

Hydrocracking Reactions

Hydrocracking reactions proceed through a bifunctional mechanism (Mills et al. 1953; Weisz 1962; Sinfeld 1964, 1983). Two distinct types of catalytic sites are required to catalyze the separate steps in the reaction sequence. The acid function provides for cracking and isomerization, and the metal function provides for olefin formation and hydrogenation. The cracking reaction requires heat, while the hydrogenation reaction generates heat. Figure 10 shows the evolution of the reactions in the hydrocracking reactor. Overall, there is a heat release during hydrocracking reactions; the heat release is a function of the hydrogen consumption, where higher hydrogen consumption will generate a larger temperature increase. Generally, the hydrogen consumption in hydrocracking is 1,200–2,400 SCFB ($200\text{--}420\text{ Nm}^3/\text{m}^3$), resulting in a typical heat release of 50–100 Btu/SCFB H_2 ($2.1\text{--}4.2\text{ kcal}/\text{m}^3\text{ H}_2$) which translates into a temperature increase of about $0.1\text{--}0.2\text{ }^\circ\text{F}/\text{SCFB}$. This amount includes the heat release generated in the hydrotreating section.

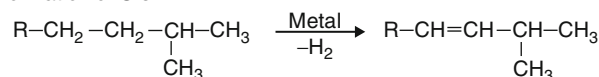
In general, the hydrocracking reaction starts with the generation of an olefin or a cycloolefin on a metal site on the catalyst. Next, an acid site adds a proton to the olefin or cycloolefin to produce a carbenium ion. The carbenium ion cracks to a smaller carbenium ion and a smaller olefin. These are the primary hydrocracking products. These primary products can react further to produce still smaller secondary hydrocracking products. The reaction sequence can be terminated at primary products by abstracting a proton from the carbenium ion to form an olefin at an acid site and by saturating the olefin at a metal site. Figure 11 illustrates the specific steps involved in the hydrocracking of paraffins. The carbenium ion typically isomerizes to form a more stable tertiary carbenium ion. Next, the cracking reaction occurs at a bond that is beta to the carbenium ion charge. The beta position is the second bond from the ionic charge. Carbenium ions can react with olefins to transfer charge from one fragment to the other. In this way, charge can be transferred from a smaller hydrocarbon fragment to a larger fragment that can better accommodate the charge. Finally, olefin hydrogenation completes the mechanism.

The hydrocracking mechanism is selective for cracking of higher carbon number paraffins. This selectivity is due in part to a more favorable equilibrium for the formation of higher carbon number olefins. In addition, large paraffins adsorb more strongly. The carbenium ion intermediate results in extensive isomerization of the products, especially to α -methyl isomers, because tertiary carbenium ions are more stable. Finally, the production of C_1 to C_3 is low because the production of these light gases involves the unfavorable formation of primary and secondary carbenium ions. Other molecular species such as alkyl naphthenes, alkyl aromatics, and so on react via similar mechanisms, e.g., via the carbenium ion mechanism.

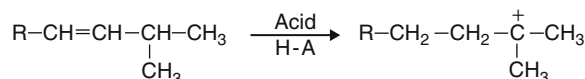
In summary, hydrocracking occurs through a bifunctional mechanism that involves olefin dehydrogenation-hydrogenation reactions on a metal site, carbenium ion formation on an acid site, and isomerization and cracking of the carbenium ion. The hydrocracking reactions tend to favor conversion of large molecules because the equilibrium for olefin formation is more favorable for large molecules and because the relative strength of adsorption is greater for large molecules. In hydrocracking, the products are highly isomerized, C_1 and C_3 formation is low, and single rings are relatively stable.

Postulated Hydrocracking Mechanism of a Paraffin

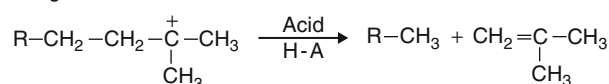
(A) Formation of Olefin



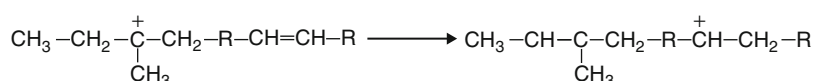
(B) Formation of Tertiary Carbeniumlon



(C) Cracking



(D) Reaction of Carbeniumlon and Olefin



(E) Olefin Hydrogenation

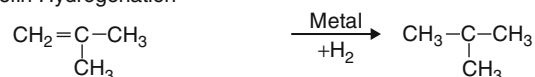


Fig. 11 Steps involved in the hydrocracking of paraffin molecules

Table 7 Thermodynamics of major reactions in hydrocracking

Reaction	Equilibrium	Heat of reaction
Aromatic saturation	Unfavorable at high temperature	Exothermic
Hydrocracking	Favorable	Exothermic
HDS	Favorable	Exothermic
HDN	Favorable	Exothermic

In addition to treating and hydrocracking, several other important reactions take place in hydrocrackers. These are aromatic saturation, polynuclear aromatics (PNA) formation, and coke formation. Some aromatic saturation occurs in the treating section and some in the cracking section. Aromatic saturation is the only reaction in hydrocracking that is equilibrium limited at the higher temperatures reached toward the end of the catalyst cycle life. Because of this equilibrium limitation, complete aromatic saturation is not when reactor temperature is increased to make up for the activity loss due to coke formation and deposition. Table 7 shows the thermodynamics of the major reactions taking place in a hydrocracker. In general, the thermodynamic equilibrium for hydrocracking is favorable. Cracking reactions, desulfurization, and denitrogenation are favored at the typical hydrocracker operating conditions. The initial step which generates an olefin or cycloolefins is unfavorable under the high hydrogen partial pressure used in hydrocracking. The dehydrogenation of the smaller alkanes is most unfavorable. Nevertheless, the concentration of olefins and cycloolefins is sufficiently high, and the conversion of these intermediates to carbenium ions is sufficiently fast so that the overall hydrocracking rate is not limited by the equilibrium olefin levels.

Polynuclear aromatics (PNA), sometimes called polycyclic aromatics (PCA), or poly-aromatic hydrocarbons (PAH) are compounds containing at least two benzene rings in the molecule. Normally, the feed to a hydrocracker can contain PNA with up to seven benzene rings in the molecule. The PNA formation is an important, though undesirable, reaction that occurs in hydrocrackers.

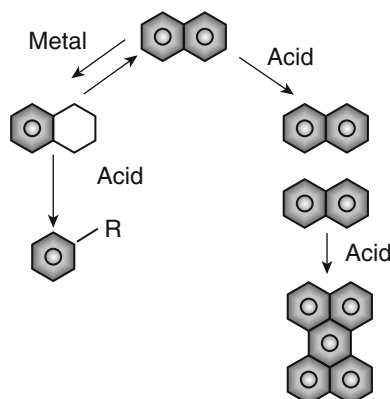


Fig. 12 Possible pathways for multi-ring aromatics

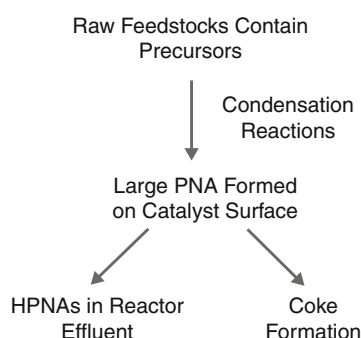


Fig. 13 HPNA formation

Figure 12 shows the competing pathways for conversion of multi-ring aromatics. One pathway starts with metal-catalyzed ring saturation and continues with acid-catalyzed cracking reactions. The other pathway begins with an acid-catalyzed condensation reaction to form a multi-ring aromatic-ring compound. This molecule may undergo subsequent condensation reactions to form a large PNA.

The consequence of operating hydrocracking units with recycled oil is the creation of large PNA molecules that can contain more than seven aromatic rings in the molecule. These are called heavy polynuclear aromatics (HPNA) whose formation is shown in Fig. 13. The HPNA produced on the catalyst may exit the reactor and cause downstream equipment fouling, or they may deposit on the catalyst and form coke, which deactivates the catalyst. Their presence results in plugging of equipment. For HPNA mitigation, a stream of 5–10 % of the unconverted material might have to be taken out of the hydrocracker, resulting in much lower than desired conversion of the feed. There is also an option available of adsorbing the HPNA materials on a bed of adsorbent, which reduces the amount of unconverted oil that is needed in the unit.

Catalysts

As stated earlier, hydrocracking catalysts are dual functional (Mills et al. 1953; Weisz 1962; Sinfeld 1964, 1983). Both metallic and acidic sites must be present on the catalyst surface for the cracking reactions to occur as well as some of the other reactions such as hydroisomerization and dehydrocyclization.

The metals providing the hydrogenation function can be noble metals (palladium, platinum) or non-noble (also called “base”) metal sulfides from group VIA (molybdenum, tungsten) and group VIIA (cobalt, nickel). As previously discussed, these metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation. The ratio between the catalyst’s cracking function and hydrogenation function can be adjusted in order to optimize activity and selectivity. For a hydrocracking catalyst to be effective, it is important that there be a rapid molecular transfer between the acid sites and hydrogenation sites in order to avoid undesirable secondary reactions. Rapid molecular transfer can be achieved by having the hydrogenation sites located in the proximity of the cracking (acid) sites.

Acid Function of the Catalyst

Cracking and isomerization reactions take place on the acidic support. Amorphous silica-alumina (ASA) provides the cracking function of amorphous catalysts and serves as support for the hydrogenation metals. Sometimes, ASA catalysts or a combination of ASA and zeolite can be used to produce high-yield distillate hydrocracking catalysts. Amorphous silica-alumina also plays a catalytic role in low-zeolite catalysts. Zeolites particularly Y and beta are commonly used in high-activity distillate-selective catalysts and in hydrocracking catalysts for the production of naphtha. Other acidic support components such as acid-treated clays, pillared clays, layered silicates, acid metal phosphates, and other solid acids have been tried in the past; however, present-day hydrocracking catalysts do not contain any of these materials.

Amorphous mixed-metal oxide supports are acidic because of the difference in charge between adjacent cations in the oxide structure. The advantages of ASA for hydrocracking are their large pores, which permit access of bulky feedstock molecules to the acidic sites, and moderate activity, which makes the metal-acid balance needed for distillate selectivity easier to obtain. Figure 14 is an illustration of silica-alumina acid sites. The substitution of an Al^{+3} cation for a Si^{+4} cation must be balanced by either a cation or by an acidic proton. The removal of water from this Brønsted acid site creates a Lewis acid site. A Brønsted acid site on a catalyst is an acid site where the acidic entity is a protonated hydrogen atom. A Lewis acid site on a catalyst is an acid site where the acidic entity is a positive ion such as Al^{+3} that can accept an electron pair, rather than a protonated hydrogen. Although plausible hydrocracking mechanisms can be written for both Brønsted and Lewis sites, Brønsted acidity is believed to be more desirable because Lewis acid sites may catalyze coke formation.

Zeolites began to be used in hydrocracking catalysts because they provided high activity due to their higher acidity compared to the ASA materials. Zeolites are crystalline aluminosilicates composed of Al_2O_3 and SiO_2 tetrahedral units that form a negatively charged microporous framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen

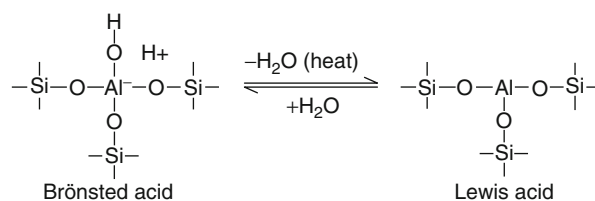


Fig. 14 Silica-alumina acid sites

atoms. Compositionally zeolites are similar to clay minerals as they are both aluminosilicates, but zeolites are crystalline and clays are not. If the mobile cations are exchanged with NH_4^+ (*ammonium ion*), followed by calcination to remove NH_3 , a Brønsted acid site is formed. With the right modification, zeolites can be tuned to provide similar yields of the desired products as ASA materials at higher activity. Mobile cations, which are not part of the framework but are part of the zeolites, are readily exchanged.

Both Brønsted and Lewis acids are possible in zeolites. The number of acid sites and the strength of the acid sites can be varied in various synthesis steps. These sites are highly uniform, but each zeolite may have more than one type of site. The following factors influence the number and strength of acid sites in zeolites:

- The types of cations occupying the ion exchange sites
- Thermal treatments of the zeolite
- The framework silica to alumina ratio in the zeolite

For example, Y zeolite can be treated to modify the Si/Al ratio; common methods to accomplish this are either a thermal or a hydrothermal treatment. In Fig. 16 is an image after hydrothermal treatment of stabilized Y zeolite. When aluminum is removed, the effect is to decrease the total number of acid sites, because each proton is associated with framework alumina. As can be seen in Fig. 16, there is also a generation of mesoporosity in the zeolite. However, the reduction of the alumina sites increases the strength of the remaining acid sites in the zeolite. As a result, the total acidity of the zeolite, which is a product of the number of sites and strength per site, peaks at an intermediate extent of dealumination. The crystallinity of the zeolite can also be modified depending on the treatment history. The acid site concentration and strength of the zeolite will affect the final hydrocracking catalyst properties. The principal advantage of zeolites for hydrocracking is their high acidity.

One zeolite used in hydrocracking, Y zeolite, is synthetic (Fig. 15). It has a structure nearly identical to the naturally found zeolite faujasite (Baerlocher and McCusker). The Y zeolite has both a relatively large free aperture, which controls access of reactants to acid sites, and a three-dimensional pore structure, which allows diffusion of the reactants in and products out with minimal interference. The structure of zeolite, beta, which is used in some hydrocracking catalysts is shown in Fig. 17 (Baerlocher and McCusker). Beta zeolite is another zeolite with a 12-ring structure, similar to faujasite; it also has a three-dimensional structure. The diffusion path length is smaller for beta than for faujasite.

Catalyst Manufacturing

Hydrocracking catalysts can be manufactured by a variety of methods. The method chosen usually represents a balance between manufacturing cost and the degree to which the desired chemical and physical properties are achieved. Although there is a relationship between catalyst formulation, preparation procedure, and catalyst properties, the details of that relationship are not always well understood due to the complex nature of the catalyst systems. The chemical composition of the catalyst plays a critical role in its performance; the physical and mechanical properties also play a major role. The preparation of hydrocracking catalysts involves several steps: precipitation, filtration (decantation, centrifugation), washing, drying, forming, calcination, and impregnation. Other steps, such as kneading or mulling, grinding, and sieving, may also be required. Depending on the preparation method used, some of these steps may be eliminated, whereas other steps may be added. For example, kneading or co-mulling of the wet solid precursors is used in some processes

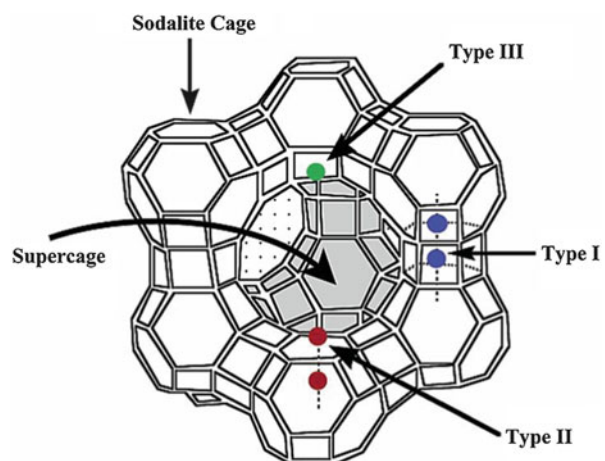


Fig. 15 Y zeolite

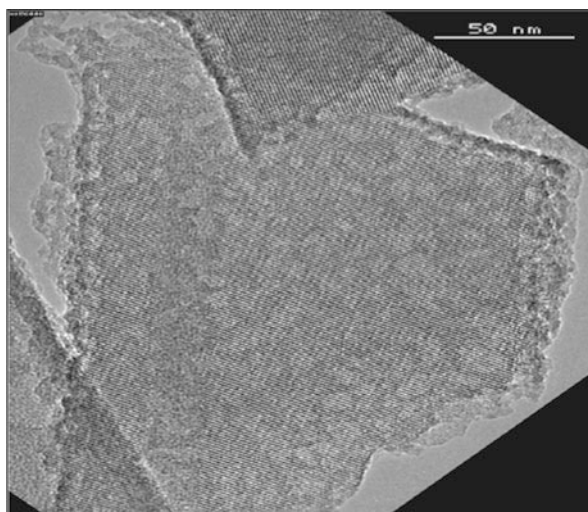


Fig. 16 Stabilized Y after hydrothermal treatment

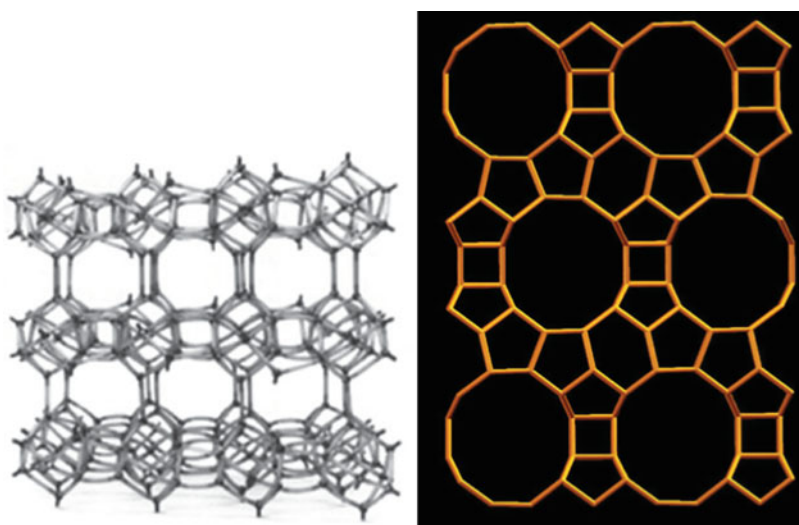


Fig. 17 Beta zeolite

instead of precipitation. When the metal precursors are precipitated or co-mulled together with the support precursors, the impregnation step can be eliminated. Described below are the steps that are an integral part of any hydrocracking catalyst manufacturing process.

Precipitation

Precipitation involves the mixing of solutions or suspension of materials, resulting in the formation of a precipitate, which may be crystalline or amorphous. Mulling or kneading of wet solid materials usually leads to the formation of dough that is subsequently formed and dried. The mulled or kneaded product is subjected to thermal treatment in order to obtain a more intimate contact between components and better homogeneity by thermal diffusion and solid-state reactions. Precipitation or mulling is often used to prepare the support for the catalyst, and the metal component is subsequently added by impregnation or incipient wetting methods.

The support characteristics determine the mechanical properties of the catalyst, such as attrition resistance, hardness, and crushing strength. High surface area and proper pore-size distribution are generally required. The pore-size distribution and other physical properties of a catalyst support prepared by precipitation are also affected by the precipitation and the aging conditions of the precipitate as well as by subsequent drying, forming, and calcining.

Forming

The final shape and size of catalyst particles are determined in the manufacturing step. Catalysts and catalyst supports are formed into several possible shapes such as spheres, cylindrical extrudates, or shaped forms such as a trilobe or a quadrilobe. Spherical catalyst support catalyst can be obtained by “oil dropping,” whereby precipitation occurs upon the pouring of a liquid into a second immiscible liquid. Other spherical processes include marmurizing. Generally, because of cost and process considerations such as pressure drop, the majority of catalysts are currently formed in shapes other than spheres. Fewer spherical catalysts are used in modern hydrocracking. Non spherical shapes are obtained by mixing raw materials to form a dough. The dough is then extruded through a die with perforations. The spaghetti-like form is then dried, calcined, and broken into short pieces. The typical length to diameter ratio of the catalyst base varies between 2 and 4. Figure 18 shows a typical extrudate support manufacturing.

The shapes of the base produced is varied. The simplest form is cylindrical, but other forms such as trilobes, twisted trilobes, or quadrilobes are also found commercially. Catalysts with multilobed cross sections have a higher surface-to-volume ratio than simple cylindrical extrudates. When used in a fixed bed, these shaped catalyst particles help reduce diffusion resistance, create a more open bed, and reduce pressure drop. Figure 19 depicts several shapes of commercial catalysts used in hydrocracking.

Drying and Calcining

Thermal treatment is applied either before and/or after impregnation of the formed catalyst. For catalysts prepared by precipitation or co-mulling of all the components (including the metal components), only drying may be required prior to forming, with subsequent calcination of the formed product. Thermal treatment of the catalyst or support eliminates water and other volatile matter. The drying and calcination conditions are of critical importance in determining the physical as well as catalytic properties of the product. Surface area, pore-size distribution, stability, attrition resistance, crush strength, and the catalytic activity are affected by the drying and calcination conditions.

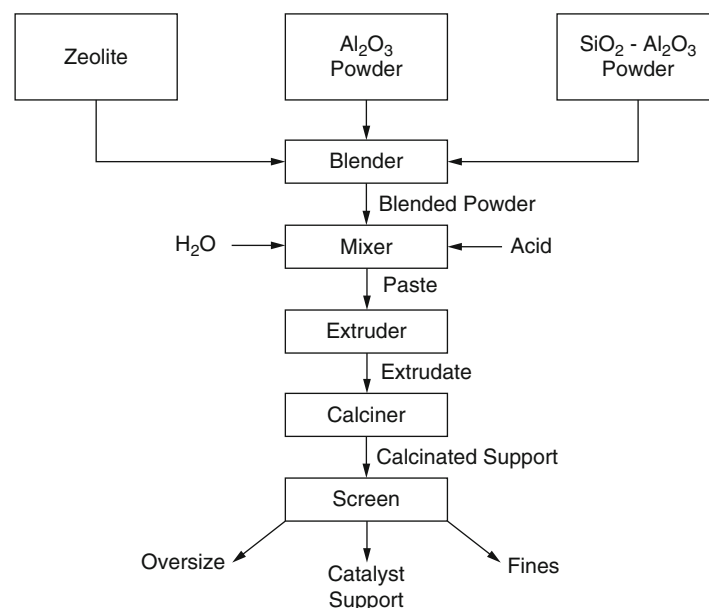


Fig. 18 Extrudate catalyst support manufacturing

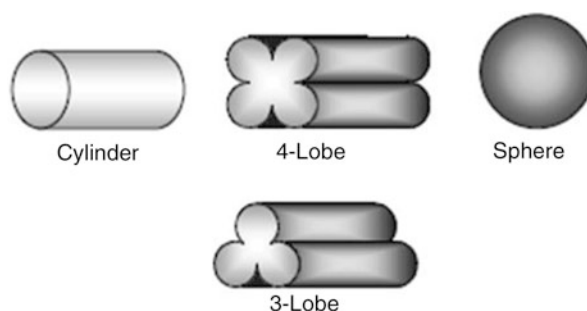


Fig. 19 Commercial catalyst shapes

Impregnation

Several methods may be used to add the active metals to the base: (a) immersion (dipping), (b) incipient wetness, and (c) evaporative. In the first method, which is the most commonly used, the calcined support is immersed in an excess of solution containing the metal compound. The solution fills the pores and is also adsorbed on the support surface. The excess solution volume is then drained off. Impregnation using incipient wetness is carried out by tumbling or spraying the activated support with a volume of solution having the concentration of metal compound proportioned to get the targeted metal level, and equal to or slightly less than the pore volume of the support. The metal-loaded support is then dried and calcined. Metal oxides are formed in the process; the calcination step is also called oxidation. In evaporative impregnation, the support is saturated with water or with acid solution and immersed into the aqueous solution containing the metal compound. That compound subsequently diffuses into the pores of the support through the aqueous phase. Figure 20 shows an example of catalyst finishing (impregnation).

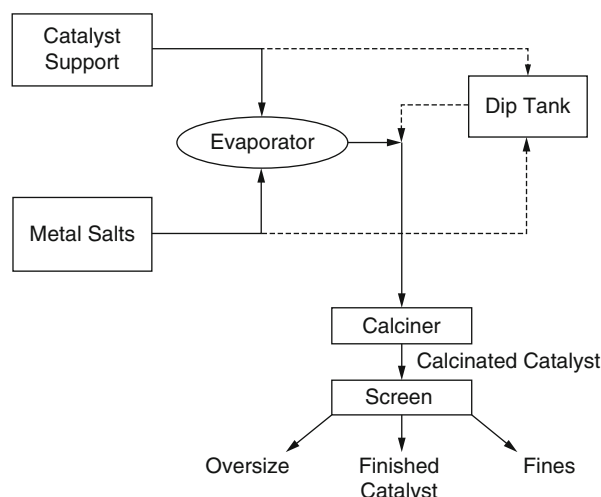


Fig. 20 Example of metal loading the catalyst base

Catalyst Loading (Reactor) and Activation of the Catalyst

Catalyst Loading into Reactor

There are two methods of catalyst loading, sock loading and dense loading. Sock loading is done by pouring the catalyst into a hopper mounted on top of the reactor and then allowing it to flow through a canvas sock into the reactor. Dense loading or dense bed packing is done with the help of a mechanical device. The dense loading method was introduced in the mid-1970s. Catalyst loaded by sock loading will have a higher void fraction than catalyst that was dense loaded. Dense bed packing and the resulting higher-pressure drop provide a more even distribution of liquid in a trickle-flow reactor. Most distillate hydrocrackers are in the trickle-flow regime. If diffusion limitations are negligible, dense loading is desirable in order to maximize the catalyst mass per volume of the reactor and, thus, the reaction rate per unit reactor volume. Another advantage of dense loading is that it orients the catalyst particles in a horizontal and uniform manner. This improves the vapor/liquid distribution through the catalyst beds. Catalyst particle orientation is important especially for cylindrically shaped extruded catalyst in vapor/liquid reactant systems. When the catalyst particles are oriented in a horizontal position in the catalyst bed, liquid channeling is almost completely eliminated. Poor liquid distribution tends to occur when the catalyst loading is done by the sock loading method, which generally causes the extrudates to be oriented in a downward slant toward the reactor walls, increasing bed voids and creating poor liquid distribution. Of all the factors influencing catalyst utilization, catalyst loading has generally proven to be a very important factor. Except for the hydrocrackers that have reactor pressure drop limitations mainly due to operation at higher than design throughputs, the great majority of units worldwide are dense loaded.

Today catalysts are most commonly loaded in a particular sequence so that the overall reactor can run most efficiently. The reactor loading is done in a way to protect the hydrotreating and hydrocracking catalysts. After the inlet distributor tray, a catalyst bed is loaded that will remove particulates and has been formulated to trap the metals and particulate that are present in the feed. This method of loading is called an activity and particle size-graduated loading or “graded bed” and is depicted in Fig. 21. The graded bed materials are large and an example of graded bed materials is shown in Fig. 22.

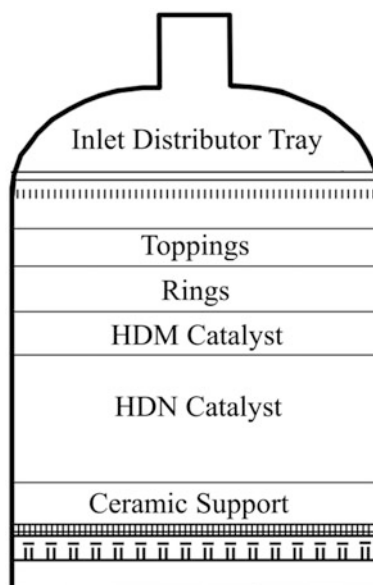


Fig. 21 Example of the graded bed

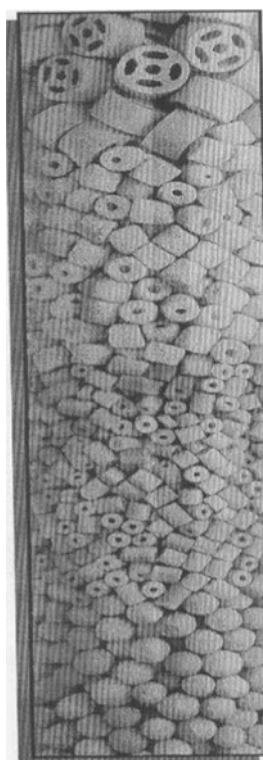


Fig. 22 Images of graded bed catalysts

Catalyst Activation

Base metal hydrocracking catalysts have to be prepared in the final state through a sulfiding procedure in order to create the active species, the metal sulfides. Several names are used for this treatment, such as sulfiding, pre-sulfiding, and pre-sulfurizing in addition to the term activation. The

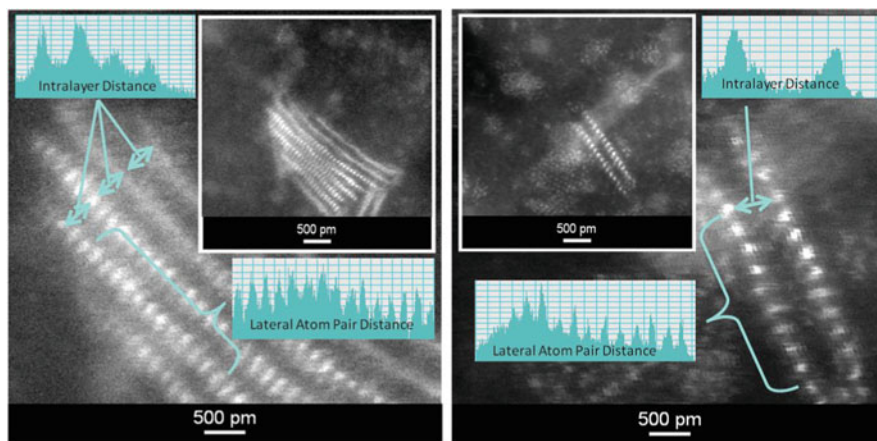


Fig. 23 Image of NiWS active phase using aberration-corrected Titan 80–300 Super X electron microscope

metals on the greatest majority of catalysts are in an oxide form at the completion of the manufacturing process.

The noble metal catalysts are activated by hydrogen reduction of the finished catalyst, in which the metal is also in an oxide form. Calcination in air prior to reduction is necessary to avoid metal sintering. The presence of water vapors is generally avoided, also to prevent metal sintering. By using an excess of hydrogen, the water formed during reduction can be swept away. The activation of noble metal catalysts by hydrogen reduction occurs at 570–750 °F (300–400 °C).

The active phase is similar for the CoMo or NiMo supported on Al_2O_3 or SiO_2 and by analogy Ni/W on the more complex hydrocracking catalyst (Topsoe et al. 1996). These consist of Co or Ni atoms on the edges of MoS_2 slabs and are referred to as CoMoS and NiMoS phases, and by analogy NiWS phase. W and Mo exhibit different behavior with respect to sulfidation. Ni/W is more difficult to sulfide than Ni/Mo, i.e., requires higher temperature. The presence of the Ni enhances the sulfidation of either Ni or Mo. The slabs of Mo or S have a specific length and appear as strands with different levels of stacking. An image (Bricker et al. 2012) of Ni/W in a hydrocracking catalyst is shown in Fig. 23. In this figure the individual atoms of W can be seen.

The non-noble (base metal) catalysts are activated by transforming the catalytically inactive metal oxides into active metal sulfides. This is accomplished mainly in situ though some refiners have started to do the activation outside the unit (ex situ). More and more refiners will opt to receive the catalyst at the refinery site in pre-sulfided state to accelerate the start-up of the unit. In situ sulfiding can be accomplished either in vapor or liquid phase. In vapor phase sulfiding, the activation of the catalyst is accomplished by injecting a chemical which easily decomposes to H_2S , such as dimethyl disulfide (DMDS) or dimethyl sulfide (DMS). The use of H_2S was fairly common until a few years ago, but now it is only rarely used because of environmental and safety concerns. Liquid-phase sulfiding can be accomplished with or without the addition of organo-sulfur compounds such as DMDS in the feedstocks. In the latter case, the feedstock is generally a gas oil-type material that contains sulfur compounds in ranges from a few thousand to 20,000 ppm. The H_2S necessary for the activation of the catalyst is generated by the decomposition of the sulfur compounds.

In the 1960s and early 1970s, the preferred sulfiding procedure in the industry was liquid phase with a sulfur-containing compound such as DMDS or DMS. The addition of the sulfur compounds resulted in saving time when compared to either vapor phase or liquid phase without spiking agents. Another advantage of liquid-phase over gas-phase sulfiding is that all the catalyst particles were wet from the beginning of the catalyst life; there was a small chance of catalyst bed channeling which can

occur if the catalyst particles are allowed to dry out. In situ sulfiding occurs at temperatures between 450 °F and 600 °F (230–315 °C) regardless of the method used. Some catalyst manufacturers recommend the sulfiding be conducted at full operating pressure, while others prefer it be done at pressures lower than the normal operating pressure. Ammonia injection is practiced during the sulfiding of high-activity (high zeolite content) catalysts to prevent premature catalyst deactivation.

In the case of ex situ pre-sulfurization of catalyst, sulfur compounds are loaded onto the catalyst. The activation occurs when the catalyst, which has been loaded in the reactor, is heated up in the presence of hydrogen. The activation can be conducted either in vapor or liquid phase. Generally, activation of ex situ pre-sulfurized catalyst is accomplished faster than if the sulfiding is done in situ; however, there is the additional expense due to the need for the ex situ pre-sulfurization step. The economics vary from refiner to refiner; however, ex situ pre-sulfurization is rarely used for hydrocracking catalysts.

Catalyst Deactivation

Catalyst deactivation is the gradual loss of the catalyst's activity to convert the feed conversion. In practical terms, it is the temperature required to obtain a fixed conversion. As the run progresses, the catalyst loses activity. Catalyst will lose activity in several ways described below.

Catalyst Coking

Coke deposition is a by-product of the cracking reactions. The deposition of coke on a catalyst is a function of time and temperature. The longer the catalyst is in service and/or the higher the temperature of the process, the deactivating effect will be more severe. The coking of the catalyst begins with the adsorption of high-molecular-weight, low hydrogen/carbon ratio ring compounds; it proceeds with further loss of hydrogen content and ends with varying degrees of hardness of coke. This coke can cover active sites and/or prevent access to these sites by physical blockage of the entrance to the pores leading to the sites. Coke is not a permanent poison. Catalyst, which has been deactivated by coke deposition, can be, relatively easily, restored to near original condition by regeneration.

Reversible Poisoning/Catalyst Inhibition

Catalyst poisoning is primarily the result of strong chemisorption of impurities on active sites. Hydrocracking catalysts in a first-stage reaction environment such as once-through or single-stage configuration have to operate with high concentrations of both NH_3 and H_2S in the gas phase. This type of poisoning is reversible, i.e., when the deactivating agent is removed, the deactivating effect is gradually reversed. It is possible that if the catalyst temperature is raised, it can compensate for the deactivating effects. However, raising temperatures has to be done cautiously since the rate of coke deposition will accelerate. For example, NH_3 will adsorb strongly on the acidic sites of the catalysts. If there is a temporary exposure to high ammonia, the catalyst will require higher temperature to maintain activity. However, if the NH_3 concentration lowers to the more typical value, the catalyst should return to the normal activity as the ammonia desorbs from the surface. Another example of a reversible poison is carbon monoxide, which can impair the hydrogenation reactions by preferential adsorption on active metal sites. Another example is H_2S , which in moderate to high concentrations can reduce the desulfurization rate constant. In this case, the removal of H_2S from the recycle gas system solves the problem.

Catalytic Metal Agglomeration

Another reversible form of catalyst deactivation is the agglomeration of the hydrogenation component of the catalyst. It can be caused by poor catalyst activation conditions in which a combination of high water partial pressure and high temperature may exist for a prolonged period. Regeneration can restore the catalyst to near original condition.

Non-catalyst Metals Deposition

Some metals may come into the system via additives, such as silicon compounds used in delayed coking unit coke drums to reduce foaming, or feed contaminants such as Pb, Fe, As, P, Na, Ca, and Mg, or as organometallic compounds in the feed primarily Ni and V. Ni and V deposition occurs at the pore entrances and near the outer surface of the catalyst, creating a rind layer which effectively chokes off the access to the interior part of the catalyst, where most of the surface area resides. Metal deposition can damage the acid sites, the metal sites, or both. Deposition of metals is not reversible even with catalyst regeneration.

Catalyst Support Sintering

Catalyst support sintering is another reason for loss of catalyst activity and it also is irreversible. Sintering is also a result of high temperatures and particularly in connection with high water partial pressures. In this case the catalyst support material can lose surface area from a collapse of pores or from an increase in the diameter of pores, with the pore volume remaining approximately constant.

Catalyst Regeneration

A coked catalyst is usually regenerated by combustion in a stream of diluted oxygen or air, although steam or steam-air mixtures have also been used in the past. Upon combustion, coke is converted to CO_2 and H_2O . In the absence of excess oxygen, CO may also form. Except for the noble metal catalysts, hydrocracking catalysts contain sulfur, as the metals are in a sulfide form. In the regeneration process, the sulfur will be emitted as SO_2 . In general, sulfur oxide emission starts at lower temperature than CO_2 emission. Regeneration of commercial catalysts can be done in situ or ex situ. The majority of commercial catalyst regeneration is performed ex situ because of environmental considerations. Several companies operate ex situ regeneration by using different equipment for burning off the coke. One company uses a continuous rotolouver, which is a cylindrical drum rotating slowly on a horizontal axis and enclosing a series of overlapping louvers. The spent catalyst passes slowly through the rotolouver, where it encounters a countercurrent of hot air. Another company uses a porous moving belt as a regenerator. The catalyst is moved with the stainless steel belt through a stationary tunnel furnace vessel where the regeneration takes place. Yet a third regeneration company uses ebullated bed technology to perform the catalyst regeneration. Regardless of the regeneration process, the spent catalyst is submitted to de-oiling prior to regeneration. This is to eliminate as much hydrocarbon as possible as well as to remove as much sulfur as possible to prevent formation of sulfates which could deposit on the catalyst and not be removed during regeneration. Sulfates are deleterious to catalyst performance.

Hydrocracking Process Variables

The proper operation of the unit will depend on the careful selection and control of the processing conditions. By careful monitoring of these process variables, the unit can operate to its full potential.

Catalyst Temperature

The amount of conversion which takes place in the reactors is going to be determined by several variables: the type of feedstock, the amount of time the feed is in the presence of the catalyst, the partial pressure of hydrogen in the catalyst bed, and, most importantly, the temperature of the catalyst and reactants. A high temperature in the reactor causes a fast rate of reaction and, therefore, the high the conversion. Since hydrocracking is exothermic, overall, the temperature increases as the feed and recycle gas proceed through any particular catalyst bed. Maintaining temperature control at all times is very important. More heat can be generated from the reactions than the flowing streams can remove from the reactors. If this happens, the temperature may increase very rapidly. This condition is called a temperature excursion or a temperature runaway. A temperature runaway is a very serious situation since extremely high temperatures can be generated within a short period of time. These high temperatures can cause damage to the catalyst and/or to the reactors. To avoid these situations, temperature guidelines have to be observed. These guidelines are dependent on the type of feedstock, and the type of catalyst, and vary from catalyst supplier to catalyst supplier. But by and large, the temperature rise of catalyst beds loaded with noble metal catalyst is limited to about 30 °F (17 °C). The temperature rise of catalyst beds loaded with high-activity base metal catalysts (for naphtha production) is limited to about 25 °F (14 °C), and of those loaded with low-zeolite content catalyst (for middle distillate production), the temperature rise is limited to 40 °F (22 °C). Finally, maximum bed temperature rises of about 50 °F (28 °C) are recommended for amorphous catalysts. The maximum bed temperature rise of 50 °F (28 °C) is also recommended for most pretreating reactors. To properly monitor the reactions as the reactants pass through the catalyst bed, measuring the temperature of the flowing stream at the inlet and outlet of each bed and/or the reactor is not sufficient. The temperature at the inlet, outlet, and radially throughout the catalyst bed must be observed. A temperature profile plot is a useful tool for evaluating performance of catalyst, effectiveness of quench, and reactor flow patterns. A temperature profile can be constructed by plotting the catalyst temperature versus distance into the catalyst bed or more accurately plotting catalyst temperature against the weight percent of catalyst. The hydrocracking reactor should be operated with equal catalyst peak temperatures for attaining the maximum catalyst operating cycle length. In this manner the total catalyst volume is utilized during the entire cycle. The weight average bed temperature (WABT) is typically used to compare the catalyst activity. Figure 24 gives a general description of how the WABT is calculated for a reactor.

The rate of increase of the reactor WABT to maintain both hydrotreating and hydrocracking functions, in order to obtain the desired conversion level and product quality, is referred to as the deactivation rate. It is one of the key variables used to monitor the performance of the catalyst systems. The deactivation rate can be expressed in °F per barrel or cubic meter of feed processed per pound or kilogram of catalyst (°C per m³ of feed per kilogram of catalyst) or more simply stated as °F per day (°C per day). The decrease in catalyst activity for hydrotreating catalyst will show up in a decrease in its ability to maintain a constant nitrogen level in the hydrotreating catalyst effluent. For hydrocracking catalyst, a decrease in catalyst activity will generally show up in its ability to maintain a constant conversion to the desired product slate. To hold the same conversion level to the desired product slate, the reactor WABT is gradually increased.

Conversion

Conversion is useful as a measure of the severity of the operation. The operation requires higher severity as indicated by higher catalyst temperature to go to higher conversion levels and higher severity to reduce the endpoint of the product at a constant conversion. Conversion is normally controlled by catalyst temperature.

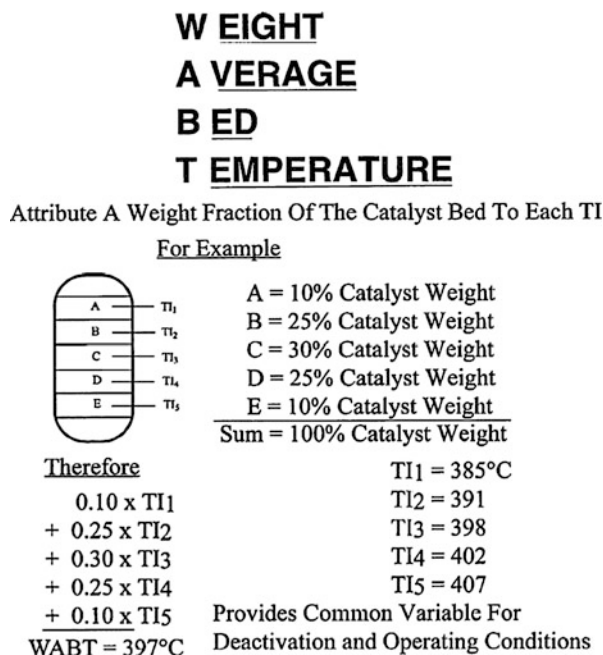


Fig. 24 Calculation of weighted average bed temperature (WABT)

The term “gross conversion” is usually defined as

$$\text{Gross Conversion, vol\%} = (\text{Fresh Feed} - (\text{Fractionator Bottoms}) / \text{Fresh Feed}) \times 100$$

where

Fresh feed = fresh feed rate, barrels per day (BPD) or m³/h

Fractionator bottoms = net fractionator bottoms product to storage, BPD or m³/h

Fresh Feed Quality

The quality of the raw oil charged to a hydrocracker will affect the temperature required in the catalyst bed to reach the desired conversion, the amount of hydrogen consumed in the process, the length of time before the catalyst is deactivated, and the quality of products. The effect of the feedstock quality on the performance of the unit is important and should be well understood, especially with regard to contaminants that can greatly reduce the life of the catalyst.

Sulfur and Nitrogen Compounds

In general, increasing the amount of organic nitrogen and sulfur compounds contained in the feed results in an increase in the severity of the operation. The sulfur content of the feed for a normal vacuum gas oil charge stock can be as high as 2.5–3.0 wt%. The higher sulfur levels will cause a corresponding increase in the H₂S content of the recycle gas that will normally have little or no effect on catalyst activity.

The organic nitrogen compounds, which are converted to ammonia, compete with the hydrocarbon for the active catalyst sites. This results in a lower apparent activity of the catalyst as the ammonia concentration increases. Consequently feedstocks with high organic nitrogen contents are more difficult to process and require higher catalyst temperatures or higher catalyst volumes.

Hydrogen Content

The amount of unsaturated compounds (such as olefins and aromatics) contained in the feed will have an effect on the heat released during the reaction and on the total hydrogen consumption on the unit. In general, for a given boiling range feedstock, a reduction in API gravity (increase in specific gravity) indicates an increase in the amount of unsaturated compounds and, therefore, higher heats of reaction and higher hydrogen consumption. Large amounts of unsaturated hydrocarbons can also cause a heat balance problem if the unit has not been designed to process that type of feed.

Boiling Range

The typical charge stock to a hydrocracker for distillate production is a 700 °F+ (370 °C+) boiling range vacuum gas oil or other feedstocks with similar boiling ranges such as heavy coker gas oil from a delayed coming unit. Increasing the boiling range usually makes the feed more difficult to process which can lead to higher catalyst temperatures and shorter catalyst life. This is especially true if the feed quality is allowed to decrease significantly due to entrainment of catalyst poisons in the feed. Higher endpoint feeds also usually have higher sulfur and nitrogen contents, which again make a feedstock more difficult to process.

Cracked Feed Components

Cracked feedstocks derived from catalytic cracking or thermal cracking can also be processed in a hydrocracker. These cracked components tend to have higher contaminants such as sulfur, nitrogen, and particulates. They are also more refractory, with high aromatics content and PNA precursors. These compounds make cracked stocks harder to process and harder to produce quality products.

Permanent Catalyst Poisons

Organometallic compounds contained in the feed will be decomposed, and the metals will be retained on the catalyst, thus decreasing its activity. Since metals are normally not removable by oxidative regeneration, once metals have poisoned a catalyst, its activity cannot be restored. Therefore, metal content of the feedstock is a critical variable that must be carefully controlled. The particular metals which usually exist in vacuum gas oil-type feeds are naturally occurring nickel, vanadium, and arsenic as well as some metals which are introduced by upstream processing or contamination such as lead, sodium, silicon, and phosphorous. Iron naphthenates are soluble in oil and will be a poison for the catalyst. Iron sulfide as corrosion product is normally not considered a poison for the catalyst and is usually omitted when referring to total metals.

The tolerance of the catalyst to metals is difficult to quantify and is somewhat dependent upon the type of catalyst being employed and the severity of the operation, i.e., the higher the severity, the lower will be the metals' tolerance since any impairment of activity will affect the ability to make the desired conversion. It is recommended to keep the total metals in the feedstock as low as possible and protect active catalyst by the use of catalysts designed to remove metals and graded bed strategies.

Fresh Feed Rate (LHSV)

The amount of catalyst loaded into the reactors is based upon the quantity and quality of the design feedstock and the desired conversion level. The variable that is normally used to relate the amount of catalyst to the amount of feed is termed liquid hourly space velocity (LHSV). LHSV is the ratio of volumetric feed rate per hour to the catalyst volume. Space velocity is the inverse of space time or the residence time the feed resides over the catalyst. Hydrocrackers are normally designed for an LHSV that depends on the severity of the operation. Increasing the fresh feed rate with a constant catalyst

volume increases the LHSV, and a corresponding increase in catalyst temperature will be required to maintain a constant conversion. The increased catalyst temperature will lead to a faster rate of coke formation and, therefore, reduce the catalyst life. If the LHSV is run significantly higher than the design of the unit, the rate of catalyst deactivation may become unacceptable. LHSV can be defined as

$$\text{LHSV hr}^{-1} = \frac{\text{Total Feed to Reactor Inlet, m}^3/\text{hr}}{\text{Total Catalyst volume, m}^3}$$

Liquid Recycle

Some hydrocrackers are designed to recycle oil from the product fractionator bottoms back to the reactors. This recycled oil stream is normally material distilled below the heaviest fractionator side-cut product. For a distillate-producing hydrocracker, the recycle stream is normally a 600–700 °F (315–370 °C) heavy diesel plus material.

The liquid recycle rate is normally adjusted as a ratio with fresh feed. This variable is called combined feed ratio (CFR) and is defined as follows:

$$\text{CFR} = \frac{\text{Fresh Feed Rate} + \text{Liquid Recycle Rate}}{\text{Fresh Feed Rate}}$$

If the unit has no liquid recycle from the fractionator back to the reactors, the CFR is 1.0, and the unit is said to operate in a once-through mode. If the amount of liquid recycle is equal to fresh feed, the CFR will be 2.0. An important function of liquid recycle is to reduce the severity of the operation. Consider conversion per pass that is defined as follows:

$$\text{Conversion per pass} = \left[\frac{\text{Feed Rate} - \text{Fractionator Bottoms Rate to Storage}}{\text{Feed Rate} + \text{Liquid Recycle Rate}} \right] \times 100.$$

If a unit were operating once through (CFR = 1.0) and 100 % of the feed were converted into products boiling below, i.e., 700 °F (370 °C), the conversion per pass is 100 % since the feed only makes one pass through the catalyst. If a unit is designed at a CFR of 2.0 and 100 % of the feed converted into products, the conversion per pass is only 50 %. In this way, as the CFR increases, the conversion per pass decreases. The catalyst temperature requirement is reduced as the CFR is increased (at a constant fresh feed conversion level) at a constant space velocity on a reactor charge basis and gas ratio. Therefore, reducing the CFR below the design value can lead to higher catalyst temperatures and shorter catalyst cycle life. Increasing the CFR above design can be helpful when operating at low fresh feed rates since it does not allow the total mass flow through the catalyst bed to reach such a low value that poor distribution patterns are established.

Hydrogen Partial Pressure

The reactor section operating pressure is controlled by the pressure that is maintained at the high-pressure separator. This pressure, multiplied by the hydrogen purity of the recycle gas, determines the partial pressure of hydrogen at the separator. The hydrogen partial pressure required for the operation of the unit is chosen based on the type of feedstock to be processed and the amount of conversion desired.

The function of hydrogen is to promote the saturation of olefins and aromatics and saturate the cracked hydrocarbons. Hydrogen is also necessary to prevent excessive condensation reactions leading to coke formation. For this reason, running the unit for extended periods of time at lower than design partial pressure of hydrogen will result in increased catalyst deactivation rate and shorter time between regeneration.

Hydrogen partial pressure has an impact on the saturation of aromatics. A decrease in system pressure or recycle gas purity has a sharp effect on the product aromatic content. This will be especially true for kerosene and diesel aromatic content, which will in turn affect the kerosene product smoke point and the diesel cetane number.

A reduction in operating pressure below its design will have a negative effect on the activity of the catalyst and will accelerate catalyst deactivation due to increased coke formation.

Operating at higher than design pressure may not be possible. There will be a practical equipment limitation on most units that will not allow significantly higher pressure than design, such as the pressure rating of the heaters, exchangers, and vessels. The major control variable for hydrogen partial pressure is the recycle gas purity that should be monitored closely to assure it is always maintained above the minimum value. The hydrogen purity can be improved by increasing the hydrogen purity of the makeup hydrogen, venting gas off the high-pressure separator, or reducing the temperature at the high-pressure separator.

Recycle Gas Rate

In addition to maintaining a prescribed partial pressure of hydrogen in the reactor section, it is equally important to maintain the physical contact of the hydrogen with the catalyst and hydrocarbon so that the hydrogen is available at the sites where the reaction is taking place. The physical contact of hydrogen with the catalyst is accomplished by circulating the recycle gas throughout the reactor circuit continuously with the recycle gas compressor. The amount of gas that must be recycled is a design variable again set by the design severity of the operation. The standard measure of the amount of gas required is the ratio of the gas being recycled to the rate fresh feed being charged to the catalyst.

As with hydrogen partial pressure, the recycle gas-to-feed ratio should be maintained at the design ratio or higher. The actual calculation for the gas-to-oil ratio can be defined as

$$\text{Gas to Oil Ratio} = \frac{\text{Total Circulating gas to reactor, SCF/day}}{\text{Total Feed to Reactor Inlet, barrels/day}} = \text{SCFB Feed}$$

As with hydrogen partial pressure, any reduction of the gas-to-oil ratio below the design minimum will have adverse effects on the catalyst life. During normal operations and throughout the cycle length, there will be a gradual increase in the reactor section pressure drop. As the pressure drop increases, there will be a tendency for the gas-to-oil ratio to decrease. When the pressure drop through the system increases to the point where the minimum gas-to-oil ratio cannot be kept, either the unit throughput will have to be decreased to bring the gas-to-oil ratio back above the minimum or the unit shutdown for catalyst regeneration or replacement. Another possibility is to increase the speed on a centrifugal compressor to overcome the increased pressure drop with the obvious limitation of the compressor's rated speed. Gas-to-oil ratio recommendations vary between licensors

and/or catalyst vendors, but in general the minimums recommended are 6,000–12,000 SCFB ($675 \text{ nm}^3/\text{m}^3$).

Makeup Hydrogen

The quality of the hydrogen-rich gas from the hydrogen plant is an important variable in the performance of hydrocrackers since it can affect the hydrogen partial pressure and recycle gas-to-feed ratio and thereby influence the catalyst stability (deactivation rate). Typically pressure swing adsorption (PSA) purified hydrogen is used for high-pressure hydrocracking unit because their purity is near 100 % hydrogen. Other sources of hydrogen such as the net gas from catalytic reforming units are lower purity hydrogen and will reduce the recycle gas purity in the hydrocracking unit.

Hydrogen Purity

The purity of hydrogen in the makeup gas to a hydrocracker will have a major influence on the hydrogen partial pressure and recycle gas-to-feed ratio. Therefore, the minimum purity on the makeup gas should be set to provide the minimum recycle gas purity allowed. If the hydrogen plant is unable for some reason to produce minimum hydrogen purity product, a purge of recycle gas off the high-pressure separator may be possible to maintain the recycle gas purity requirements.

Nitrogen and Methane Content

The total of the nitrogen and methane contained in the makeup gas is only harmful as a diluent, i.e., they will reduce the hydrogen partial pressure. As long as the minimum hydrogen purity is maintained, nitrogen and methane will not affect the unit. However, it should be noted that excessive quantities of molecular nitrogen entering a hydrocracker in the makeup gas stream can cause a buildup of nitrogen in the recycle gas since the nitrogen is not condensable. If this is the case, the nitrogen will have to be removed from the reactor circuit by a small, continuous purge of recycle gas off the high-pressure separator. Nitrogen and methane, however, will increase the molecular weight of the recycle gas and increase the power requirement of the recycle gas compressor.

CO + CO₂ Content

The normal specification for CO plus CO₂ in the makeup gas stream to a hydrocracker is in the range of 20 ppm maximum. Larger quantities can have a harmful effect on catalyst activity. CO is considered the worst impurity due to the fact that it has a limited solubility in both hydrocarbon and water and will, therefore, build up in the recycle gas. CO₂, on the other hand, is much more soluble and is readily removed from the system in the high-pressure separator liquids.

Both CO and CO₂ have similar effects on the hydrocracking catalyst. They are converted on the active sites of the catalyst in the presence of hydrogen to methane and water. This methanation of CO and CO₂ competes with the normal hydrocarbon reactants for the catalyst. Therefore, if CO + CO₂ are allowed to build up, higher catalyst temperatures will be required. In an extreme case where a large quantity of CO or CO₂ would be introduced to the hydrocracker in a short period of time, a temperature excursion is theoretically possible resulting from the highly exothermic methanation reaction. A recommended practice is if the CO + CO₂ content exceeds the maximum design limit,

Table 8 Providers of hydrotreating and hydrocracking catalysts

Company	Conventional hydrocracking				Mild hydrocracking			
	HDS/ HDN	Resid	Max naphtha, jet	Max middle distillates, lubes	HDS/ HDN	Resid	Max naphtha, jet	Max middle distillates, lubes
ABB Lummus Global		x						
Advanced Refining Technology	X	x						
Albemarle	X		X	X	X			x
Axens				X	X			x
Catalyst and Chemical Industries		X	X	X				x
Chevron Lummus Global	X		X	X	X		X	X
Criterion Catalysts and Technologies	X		X	X	X		X	X
ExxonMobil Research and Engineering						X	X	
FRIPP			X	X				
Haldor Topsoe	X			X				X
Kataleuna GMBH Catalysts				X				
RIPP/Sinopec				X				
UOP			X	X				X
Zeolyst International (marketed by Criterion)			X	X			X	X

the catalyst temperature should not be increased to compensate for a resulting decrease in conversion. Catalyst temperature should be maintained at the same level or reduced until the problem causing the high CO + CO₂ is eliminated. In this way the catalyst will not be harmed by increased deactivation at a higher temperature, and it will also eliminate the possibility of a temperature runaway due to methanation. In addition, during reactor cooling and shutdown, the presence of CO in the recycle gas at temperatures below 200 °C can lead to formation of nickel carbonyl, which is extremely toxic and can cause death. Therefore, CO concentration should be kept as low as possible (typically less than 10 ppm).

Commercial Suppliers of Hydrocracking Process and Catalyst Technology

Various companies are able to supply the licensing technology for the hydrocracking process, and some companies specialize in the supply of catalyst (<http://www.albemarle.com/products—markets/catalyst-solutions/refinery-catalyst-solutions/clean-fuels-technologies-1629.html>; <http://france.axens.net/fr/component/axensdocuments/872/hydrocracking-brochure/english.html>; <http://www.cbi.com/technologies/technologies-serviceshydrocracking-technology>; http://www.exxonmobil.com/Apps/RefiningTechnologies/Files/sellsheet_hydrocracking.pdf; <http://www.fripp.com/en-0301020100.htm>; http://www.topsoe.com/business_areas/refining/Hydrocracking/HydrocrackingProcesses.aspx; <http://www.shell.com/global/products-services/solutions-for-businesses/globalsolutions/refinery-chemical-licensing/refining-technology.html>; <http://www.uop.com/products/catalysts/hydroprocessing/>; [Page 33 of 35](http://www.uop.com/processing-solutions/refining/vgo-</p>
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[fuel-oil-conversion/](#); <https://grace.com/catalysts-and-fuels/en-us/art-hydroprocessing-catalysts;http://www.criterioncatalysts.com/en/products/product-applications/hydrocracking-pretreat.html>).

The suppliers of the process technology are Axens, Chevron Lummus Global, ExxonMobil, Haldor Topsoe, Shell Global Solution, and UOP.

The providers of catalyst technology are Albemarle, Axens, Chevron Lummus Global, FRIPP, Haldor Topsoe, RIPP/Technip, and UOP.

The suppliers of the catalyst technology are shown in Table 8. There are many types of catalysts used in hydrocracking. Often combinations of catalysts are used in the units. The choice of the catalyst depends on the product slate desired by the refiner.

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A BRIEF HISTORY OF INDUSTRIAL CATALYSIS

Heinz Heinemann

June 1979

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A BRIEF HISTORY OF
INDUSTRIAL CATALYSIS

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June, 1979

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I INTRODUCTION

Industrial catalysis is an old art. Wine and soap makers have employed catalytic agents for thousands of years, though without knowledge or understanding of their workings. Large-scale conscious use of industrial catalysts originated in the mid-18th century with the introduction of the lead chamber process for manufacture of sulfuric acid, in which nitric acid was used to oxidize SO_2 to SO_3 in the presence of water. The lower oxides of nitrogen formed are in turn oxidized with air to form nitric acid. While the need for a catalyst was recognized, the scientific basis for its chemical and kinetic action came only much later. This is a trend that persists to the present. In spite of great advances in the science of catalysis, major industrial applications and novel uses have almost always been based on empirical findings. Scientific explanations followed later and frequently led to process improvements and refinements. The goal of catalytic scientists to be able to predict industrial catalytic behavior of substances and processes has thus far remained elusive. There is hope, however, that with the rapidly increasing sophistication of tools and observational means catalytic science may in the future replace catalytic art.

Mills and Cusumano^(1) have pointed out that the use of catalytic processes has grown almost exponentially from the early 18th century to the present. It has been estimated that at present over 20 percent of all industrial products have underlying catalytic steps in their manufacture. Early catalytic processes were used mostly for the production of inorganic chemicals (sulfuric acid, nitric acid, chlorine, ammonia), with catalytic processes involving organic reactions becoming prominent only in the 20th century, but rapidly dominating the industry, mostly because of the widespread application of catalysis in fuels production.

The present chapter is mostly limited to the rapid growth of industrial catalysis between the second World War and 1978. A few brief excursions into earlier history have been found necessary. The author found it difficult to ascertain exact dates for many innovations. References can in most instances be found for the time of a first commercial operation of a process, but it is much harder and in some cases impossible to determine the time of conception. In fact, the research and development leading to new technology often involves so many people and ideas that the resulting process cannot always be attributed to specific individuals. In addition, publications and even patent application dates frequently lag considerably behind conception.

The great majority of catalytic processes are still based on heterogeneous catalysis. Homogeneously catalysed processes however, have assumed much more importance in recent years and their impact is often underestimated because much of the volume and value of catalytic processes is concentrated in the petroleum refining industry which uses predominantly heterogeneous catalysts. The relative growth of homogeneous catalytic process technology is far greater in chemical and petrochemical applications than in all other industrial applications, including those of the petroleum industry.

While there has been a large number of process developments during the period under consideration, the majority are of an evolutionary type and there are relatively few process ideas that have opened up new chemistry and engineering and/or started new catalytic industries. The list presented in Table 1 gives the author's admittedly subjective impression of what might be called "breakthroughs" in catalytic technology during the last 35-40 years.

Table 1

Major Catalytic Innovations, 1935-1978

Year of first commercialization	Event	Area of industry
1936	Catalytic cracking	Petroleum
1941	Fluid-bed technology	Petroleum-petrochemicals
1942	Thermoform catalytic cracking	Petroleum
1942	Paraffin alkylation	Petroleum
1950	Catalytic naphtha reforming (Pt-catalysts)	Petroleum
1955	Ziegler-Natta polymerization	Polymers
1960	Acetaldehyde from ethylene (Wacker Chemistry)	Chemicals
1963	Low-pressure ammonia synthesis	Fertilizer
1963	Ammoxidation	Chemicals
1964	Zeolite catalysts	Petroleum-petrochemicals
1964	Oxychlorination	Monomers
1966	Olefin disproportionation	Petrochemicals
1967	Bimetallic reforming catalysts	Petroleum
1968	Shape selective catalysis	Petroleum-petrochemicals
1976	Emission control catalysts	Automotive

All of these will be discussed in this chapter along with many other developments of importance. No claim can be made for completeness.

During the early years of industrial catalysis development described in this chapter, there were several new technologies requiring extensive engineering as well as catalyst developments. Fluid catalytic cracking, catalytic reforming, and low-pressure ammonia synthesis are examples. In the last 15 to 20 years there has been more emphasis on novel catalysts that produced better products and product yields, and which could be used in existing or slightly modified equipment. Examples of this type are zeolite and bimetallic reforming catalysts. A major reason for this trend lies in the spiraling construction costs of industrial plants, with the concomitant increase in the financial risk of failure or protracted break-in periods of novel facilities. A catalyst failure at worst may require a change back to a previously used catalyst, with a loss of some days in down-time, while major equipment changes may require weeks and months during which costly facilities are nonproductive. In addition, there has been a trend to ever larger unit operations. New engineering technology is best tried in relatively small units, which however, are no longer competitive with large production facilities. One can expect the trend to improve older catalysts, and introduce novel catalysts, in existing equipment to continue for some time.

To support the importance of heterogeneous catalysis to industrial production, three tables illustrate catalytic uses: for the Petroleum Industry in the U.S.A. (Table A), giving capacities, catalyst sales and values; for the Petrochemical Industry (Table B)^x giving product volume and value; and for the Commodity Chemicals Industry (Table C)^x giving product volume and value. A similar table on industrial homogeneous catalytic uses is contained in the chapter XI (Homogeneous Catalysis, Table 5).

II CATALYTIC CRACKING AND OTHER ACID CATALYSED REACTIONS

Acid (and base) catalysis are involved in some of the oldest industrial reactions, such as hydrolysis of esters for soap manufacture and inversion of sugar cane. Friedel-Crafts reactions were discovered in 1877-1878 and aluminum chloride--a typical Friedel-Crafts type

^x Data for these tables courtesy of Catalytica Associates, Inc.

TABLE A

MAJOR APPLICATIONS OF
HETEROGENEOUS CATALYSIS IN U.S. PETROLEUM

INDUSTRY

	BBL/D	CAPACITY METRIC TONS/DAY	U. S. CATALYST SALES, MILLION LBS/YR	CATALYST VALUE MILLION \$/YEAR
1) CAT. CRACKING	5,000,000	635,000	286	143
2) CAT. HYDROCRACKING	900,000	114,000	~ 2	20
3) NAPHTHA REFORMING	2,000,000	222,000	5	27
4) CAT. ALKYLATION	890,000	85,000	3,700	128
5) CAT. HYDROTREATING	2,000,000	260,000	22	45

TABLE B

MAJOR APPLICATIONS OF HETEROGENEOUS CATALYSISIN U.S. PETROCHEMICAL INDUSTRY

	APPROXIMATE 1979 PRODUCTION (MILLION TONS/YR)	PRODUCT VALUE \$/YR IN MILLION \$
1. <u>AMMONIA SYNTHESIS</u>	15	1,500
2. <u>METHANOL</u>	4.1	693
3. <u>STEAM REFORMING</u>	6.3×10^9 SCFD	535
4. <u>OXIDATIONS</u>		
- Ethylene Oxide	2.5	1,600
- Formaldehyde	3.5	490
- Phthalic Anhydride	3.5	2,870
- Maleic Anhydride	0.2	200
5. <u>ACRYLONITRILE (AMMOXIDATION)</u>	1.0	560
6. <u>STYRENE (DEHYDROGENATION)</u>	3.8	2,660
7. <u>HYDROGENATIONS</u>		
- Aniline	0.3	274
- Cyclohexane	1.2	600
8. <u>VINYL CHLORIDE MONOMER (OXYCHLORINATION)</u>	3.5	1,050
9. <u>VINYL ACETATE MONOMER (OXYCHLORINATION)</u>	0.9	522
10. <u>BUTADIENE</u>	1.7	884

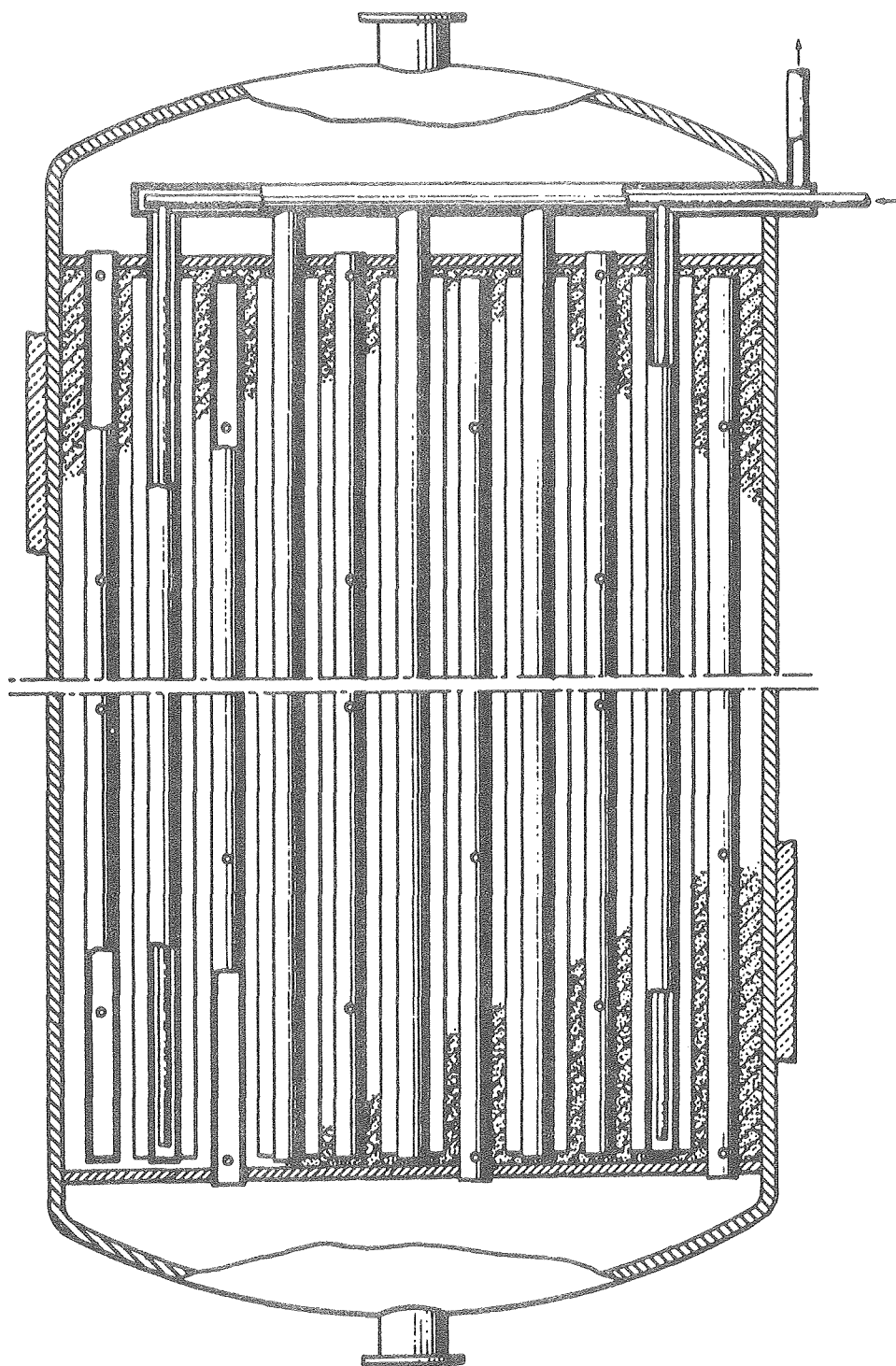
TABLE CMAJOR APPLICATIONS OF HETEROGENEOUS CATALYSTSIN COMMODITY CHEMICALS

	<u>APPROXIMATE 1979 U. S. PRODUCTION (MILLION TONS/YR)</u>	<u>PRODUCT VALUE \$/YR IN MILLION</u>
1. <u>Sulfuric Acid</u>	40	1,800
2. <u>Nitric Acid</u>	8.5	\$2,040 (pure HNO ₃)

catalyst--was the first commercial catalyst used in converting heavier petroleum hydrocarbons to lighter fragments, particularly in the gasoline boiling range.

Gasoline (boiling between 38°C and 210°C and having a $\text{C}_4 - \text{C}_{13}$ range) comprises only about 15-25% of the natural petroleum. Most of this "straight run" gasoline consists of normal or slightly branched paraffins, some naphthenes, and a few aromatics, most of these components having low octane numbers. "Cracking" of heavier petroleum fractions over selective catalysts enhances the obtainable yield of gasoline from a barrel of crude oil and results in the formation of larger quantities of highly branched paraffins, olefins, and aromatics, all of which are high octane number components. The McAfee AlCl_3 process found limited application in the years following 1915, and was operated as a batch process with a severe problem in disposing of the sludges consisting of spent aluminum chloride dissolved in hydrocarbons. Gurwitsch^(2) and Herbst^(3) observed and detailed the catalytic activity of certain activated clays as early as 1912 and 1926, respectively. A major breakthrough occurred in 1936 after Eugene J. Houdry had solved a series of problems involving catalyst deactivation, regeneration, and stability, and overcame formidable engineering problems. It is interesting to note that Houdry was a mechanical engineer who was also an automobile race driver, and as such recognized that the limitations of the internal combustion engine at that time were not of a mechanical nature but lay in the constraints imposed by the low-octane number characteristics

of gasoline then available. In searching for a better gasoline, he studied the chemistry of hydrocarbons and the synthesis of branched chain paraffins and olefins, and of aromatics, by catalytic cracking of gas oils. Houdry devised a system of cyclic reaction and regeneration which maintained the cracking unit in heat balance, and which could be practiced commercially in a continuous mode. Cyclic operation of fixed-bed cracking units, utilizing the exothermic heat of regeneration to provide the required cracking temperatures (cracking is endothermic) became a reality when Houdry Process Corporation, together with Socony-Vacuum Oil Company and Sun Oil Company, built the first commercial units at plants of the two oil companies in 1936-1938, shortly before the outbreak of the Second World War. The catalyst was contained in numerous parallel tubes that were suspended in a molten salt heat exchanger, as shown in Figure 1.^(4,5) Figure 2 shows a Houdry unit. In spite of the rapid refinements that followed, some of the original units were still in operation in the early 1960s. About 90% of the aviation gasoline base stock used in the battle of Britain came from Houdry Units.



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Fig. 1. Houdry Catalytic Cracking Unit
Reactor. Tubular catalyst containers
in molten salt medium.

Figure taken from reference 4.

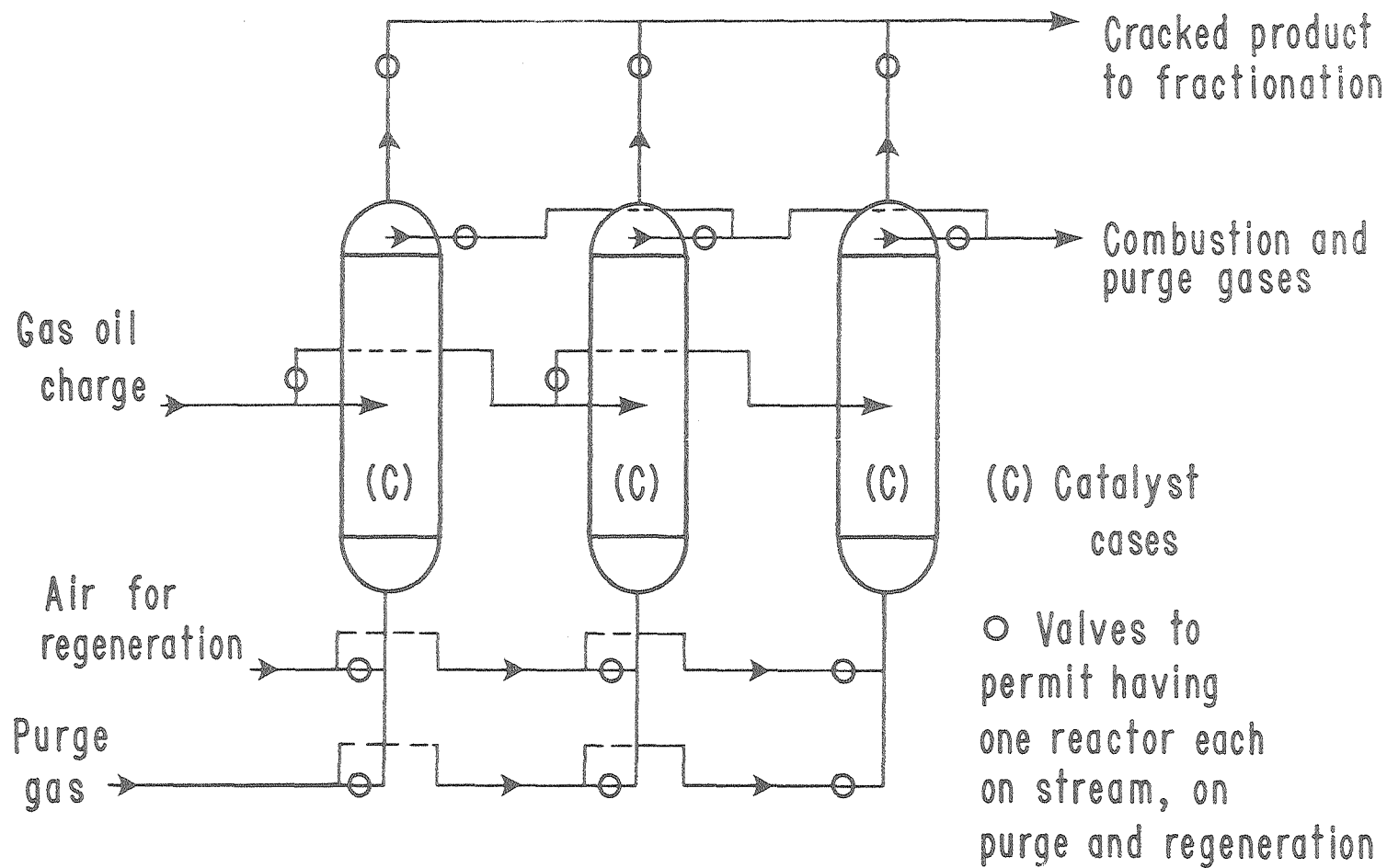


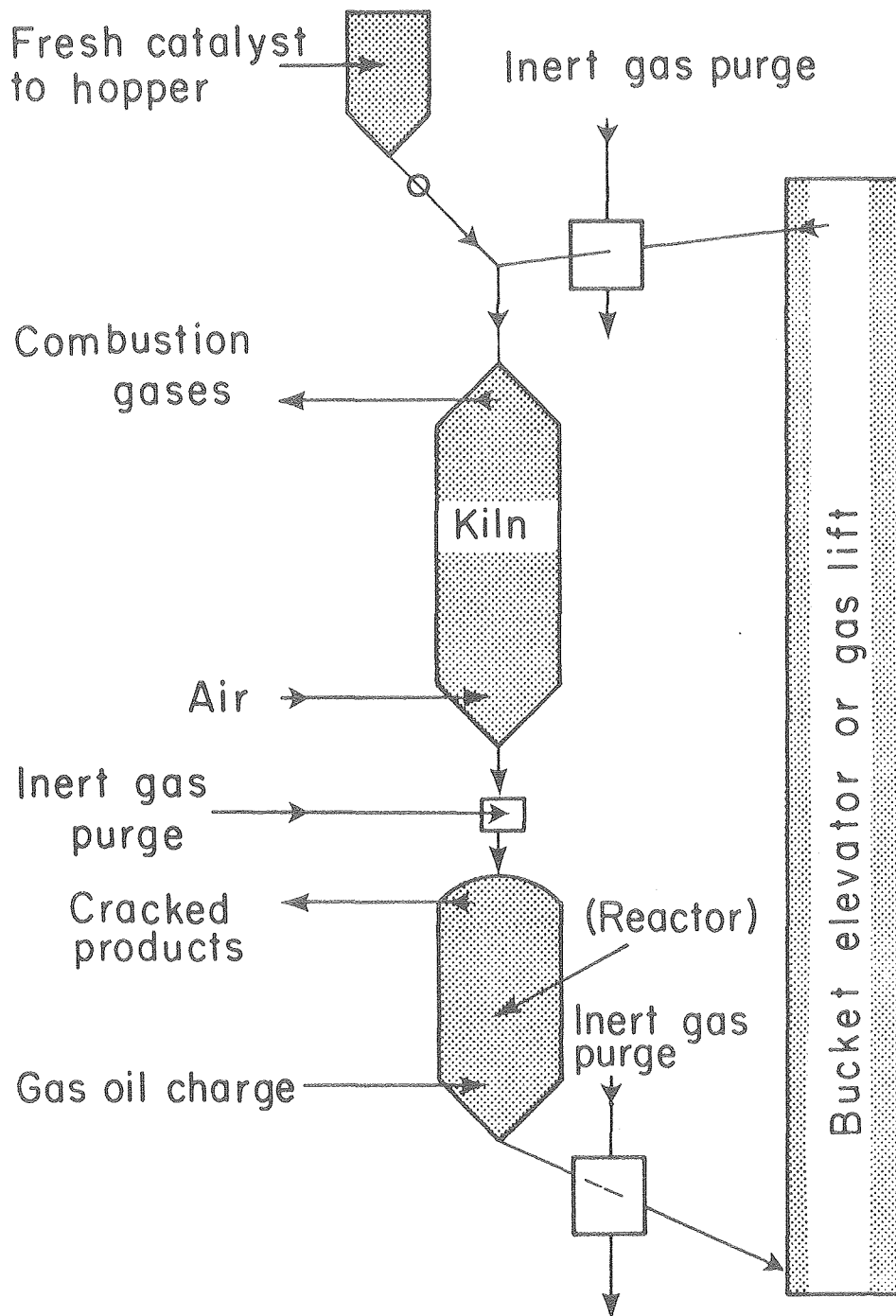
Figure 2 Schematic Drawing of Houdry Fixed Bed Catalytic Cracking Unit

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The sudden demand for large quantities of aviation gasoline during World War II accelerated the rapid expansion of the cracking process, and numerous units were built during the period from 1938 to 1950. At the same time, major improvements were made in the mechanical design of the cracking units and in the cracking catalyst.

The cyclic operation of the fixed bed units was replaced by designs which moved the catalyst continuously from a reactor through a purge zone to a regenerator, and from there through another inert gas-purge zone back to the reactor. This was accomplished by two quite different methods: In the moving-bed type of operation first introduced by Socony-Vacuum Oil Company in 1942⁽⁵⁾, the pelleted or extruded catalyst moved by gravity through reaction and regeneration zones, and was lifted from the bottom of one vessel to the top of the other by a bucket elevator (Figure 3). In the early 1950s, this design was further refined by replacing the elevator with a lift pipe in which the catalyst was blown by a high-velocity gas stream to the top vessel.⁽⁶⁾ Similar designs were commercialized by Socony-Vacuum Oil Company under the name of "Thermoform Catalytic Cracking" (TCC), and by Houdry Process Corporation under the name of "Houdriform." These units operated satisfactorily for many years, but are now gradually disappearing because their capacity is limited by heat-flow conditions. Units of larger than 20,000 bbl/day have not been built.

In 1941 a group of companies under the leadership of Standard Oil Company of New Jersey introduced the first "Fluidbed Catalytic Cracking Unit" (FCC).^(5,7) In this revolutionary design, based largely on work by Lewis and Gilleland at M.I.T., the catalyst in the form of fine particles in the 30-200 mesh range was maintained in suspension in a stream of vaporized hydrocarbons, blown through the reactor and collected in a separator and in cyclones, passed through a stand-pipe in which it was purged to the bottom of the regenerator, and blown through the regenerator by an oxygen-containing gas stream and finally returned to the reactor (Figure 4). Over the years, many improvements--such as short-contact time and



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Figure 3 Schematic Drawing of TCC Cracking Unit (Moving Bed)

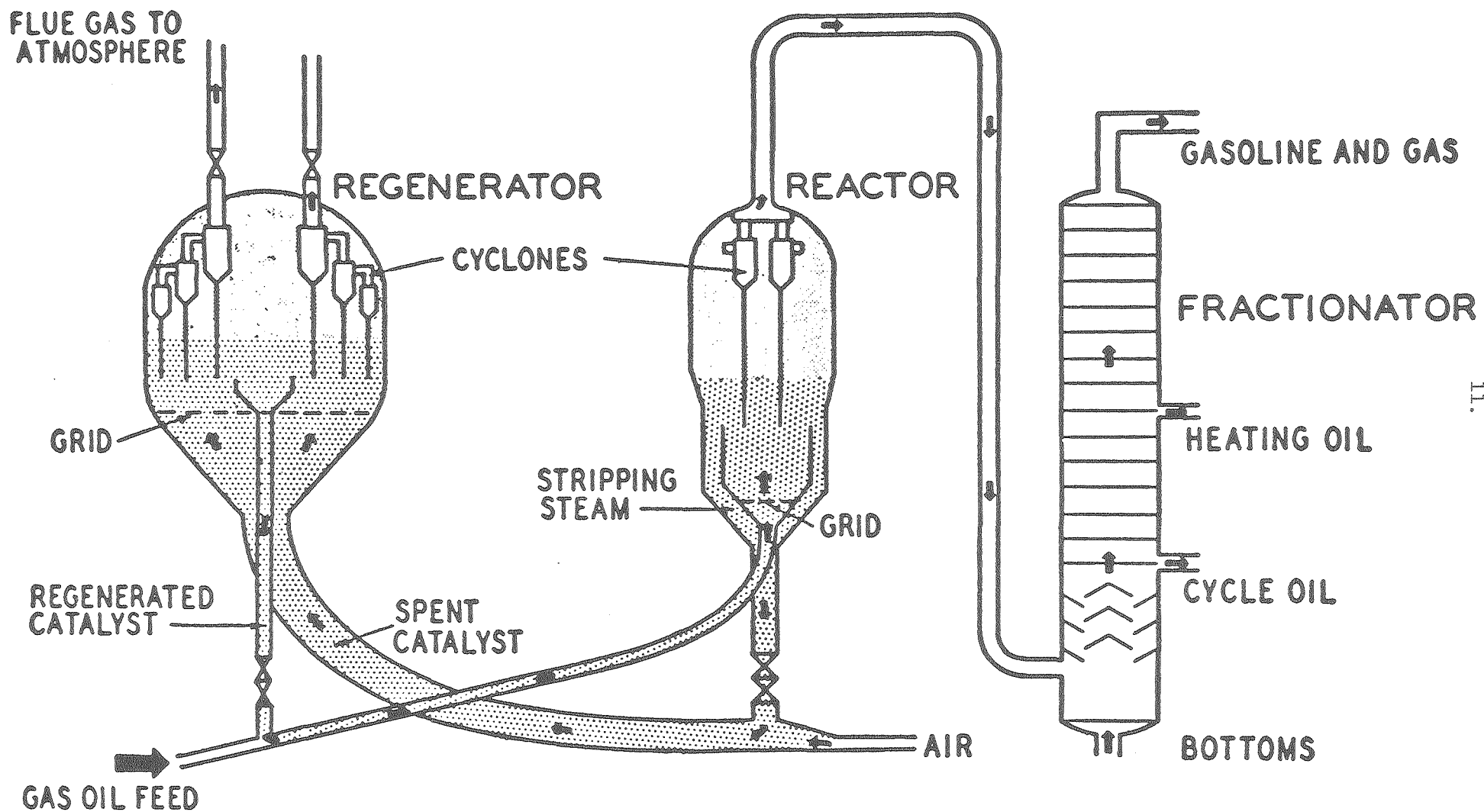
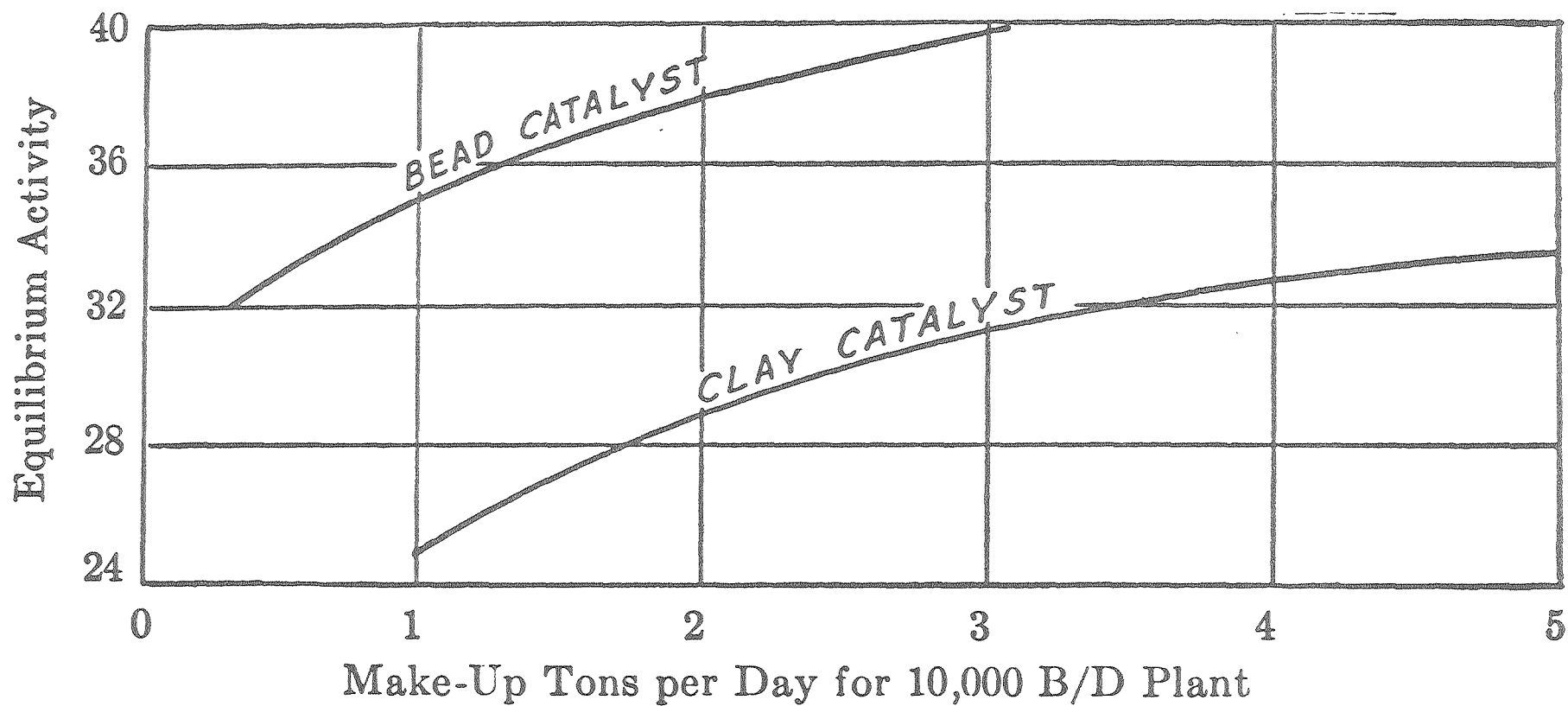


Fig. 4 Conceptual Fluid Bed Cracking Unit

riser cracking--have been made in the engineering design of FCC units. (8) Riser cracking was made possible also by improvements in the physical strength of cracking catalysts. A modern short-contact time-fluid cracker is shown in Figure 5. (8) The FCC design could be scaled to very large units because of the rapid heat exchange between carrier gas and catalyst, which permits very close temperature control. The vast majority of present cracking units are of the FCC type, and the fluid-bed technology has been applied to other processes, particularly those of a highly exothermic or endothermic nature. In 1978 the U.S. catalytic cracking capacity was about 5,000,000 bbl/day.

While these design changes were taking place, improvements were made in the catalyst type and composition. The original cracking catalysts were acid-treated clays of the montmorillonite type. They permitted larger yields of gasoline of higher octane number than had previously been obtainable by thermal cracking of gas oils. The clays were gradually replaced by amorphous synthetic silica-alumina catalysts which were more stable under regeneration conditions and also gave a better product distribution. (9) Gasoline yields obtainable from gas oil increased from about 20 percent by thermal cracking to over 40 percent with silica-alumina catalysts. The importance of the catalyst shape and pore distribution was recognized about 1945. Bead catalysts were invented by Marisic at Socony-Vacuum and resulted in lower attrition losses than pelleted or extruded catalysts in TCC-type units. The attrition and activity advances of bead versus extruded-clay catalysts is shown in Figure 6. (4) Open structure beads, produced by incorporating crystalline alumina during gelling, increased activity and reduced diffusion limitations. Variations of the silica/alumina ratio (normally 65/35) permitted fine tuning of product yields. Silica-magnesia catalysts were introduced in 1952 and resulted in better gasoline yields (but of slightly lower octane number). However, these catalysts never reached large-scale use because of regeneration problems. (10).



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Fig. 6 Activity and Make-up Rate of
Clay and Silica-alumina Bead
Catalysts
Figure taken from Reference 4.

Silica-alumina catalysts were used in FCC units as well as in TCC units, but because of the small particle size used in FCC did not require the attention to diffusional problems encountered in TCC-type units. The whole area of FCC cracking has been reviewed in detail by Venuto and Habib. (8)

A major revolution in cracking catalysts occurred in the early 1960s, and this will be described in the section on "zeolite catalysis." (III)

Leaving catalytic cracking temporarily, there are a series of other acid catalysed reactions which have become important, mostly in the fuel area. These include polymerization of olefins to dimers, trimers, and tetramers; alkylation; and isomerizations of paraffins and aromatics. All of these have been previously described in the literature, (11) and no breakthroughs have occurred in polymerization of C_3 and C_4 hydrocarbons to fuels in the last 30 years although a number of refinements have been introduced.

In alkylation to high-octane gasoline, both the sulfuric-acid and hydrofluoric-acid processes continue to dominate the field. (12)

Addition of an olefinic hydrocarbon to another molecule is being practiced in two major areas: (1) in the alkylation of isobutane with butenes or propene to produce highly branched C_7 and C_8 hydrocarbons as high octane number gasoline components; (2) in the alkylation of aromatics with ethylene or propene to produce alkyl-

aromatics. Paraffin alkylation was discovered by V. N. Ipatieff in 1935 and commercialized in 1942. The two catalysts in commercial use are sulfuric acid and hydrofluoric acid. Alkylation supplied large volumes of aviation gasoline in World War II. The subject has been reviewed by R. M. Kennedy^(11) and others and improvements in the process technology since then do not involve major inventions.

Alkylation of aromatics with olefins is used primarily in the production of ethylbenzene and of cumene. Anhydrous $\text{AlCl}_3 + \text{HCl}$ catalysts have been used since the early 1940ties. A major improvement in catalyst technology was introduced in 1977 by the use of zeolites and will be discussed in the section on zeolites. It has eliminated the problems of acid sludge erosion.

In aromatics alkylation and aromatics isomerization, novel process technology has emerged which will also be described in the section on zeolites.

The need for paraffin isomerization arose during World War II. Alkylation was one of the few routes to high-octane-number aviation gasoline. While sufficient amounts of C_4 olefins were available from catalytic and thermal cracking, there was a shortage of isobutane. On the other hand, there were supplies of n-butane which could be isomerized. Two routes, commercialized by Shell Oil Company and Texaco in 1941 were used for isomerization of normal to isobutane. Both were based on aluminum chloride as a catalyst and gaseous HCl as a promoter.^(13) Over 40 units were built. In one process, a

sludge of AlCl_3 in aromatic hydrocarbons served as a catalytic liquid through which the n-butane gas was passed; in the other, anhydrous AlCl_3 was deposited on alumina or on bauxite, and the process was operated in a fixed-bed configuration. The major problem with both processes was the highly corrosive nature of the sludge or of the sludge drippings from the solid catalyst. Frequent reactor replacement was required. Paraffin isomerization, previously dependent on AlCl_3 -type catalysis, has since then made progress by the introduction of dual functional catalysts, described in another section.⁽¹⁰⁾ The newer processes have concentrated on C_5 rather than C_4 hydrocarbons.

III ZEOLITE CATALYSIS

Crystalline alumino silicates possessing base exchange properties have been known for well over 100 years and occur quite frequently in nature. They have found early application in ion-exchange chemistry, but their catalytic usefulness was discovered only in the late 1950s. Early attempts to use them as a base for catalytic cracking failed, and for a long time it was believed that the regular and uniform pore structure of a crystalline material was inferior to the pore-size distribution of amorphous catalysts. In the mid-1950s Union Carbide Corporation first commercially produced synthetic zeolites of the x and y type (faujasites) as adsorbents; (Fig 7.) they later became ingredients of zeolite catalysis. While Rabo et al. pointed out in 1960⁽¹⁴⁾ that these materials possessed activity for such reactions as isomerization, it remained for Plank and Rosinsky at Socony-Mobil Oil Corporation to stabilize zeolites x and y so that they could withstand regeneration temperatures and steam partial pressures occurring in cracking without sintering and losing crystallinity. They achieved this by ion exchanging rare earth metals for alkali metals, and using a matrix of silica-alumina^(15,16) to separate zeolite crystallites.

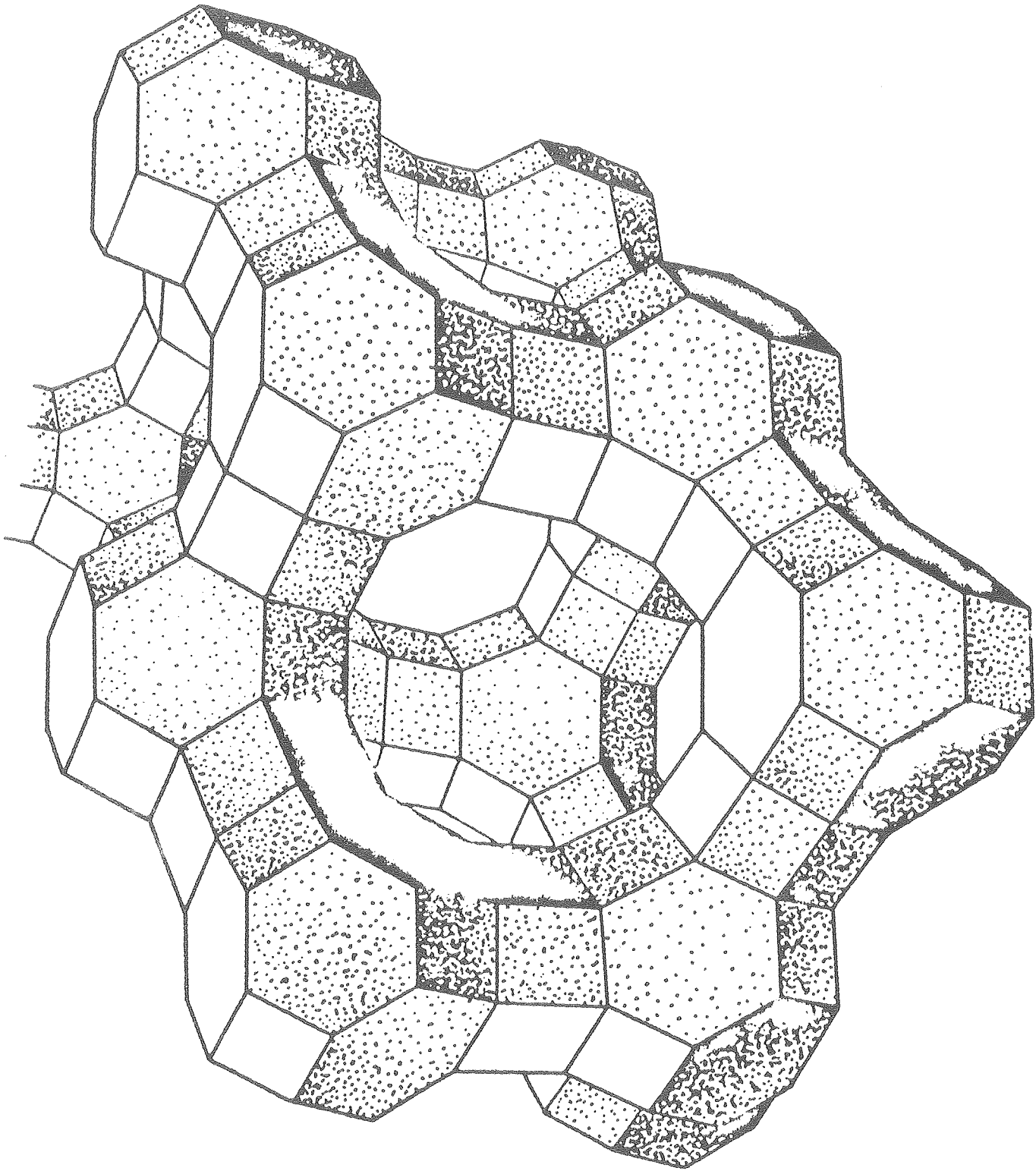
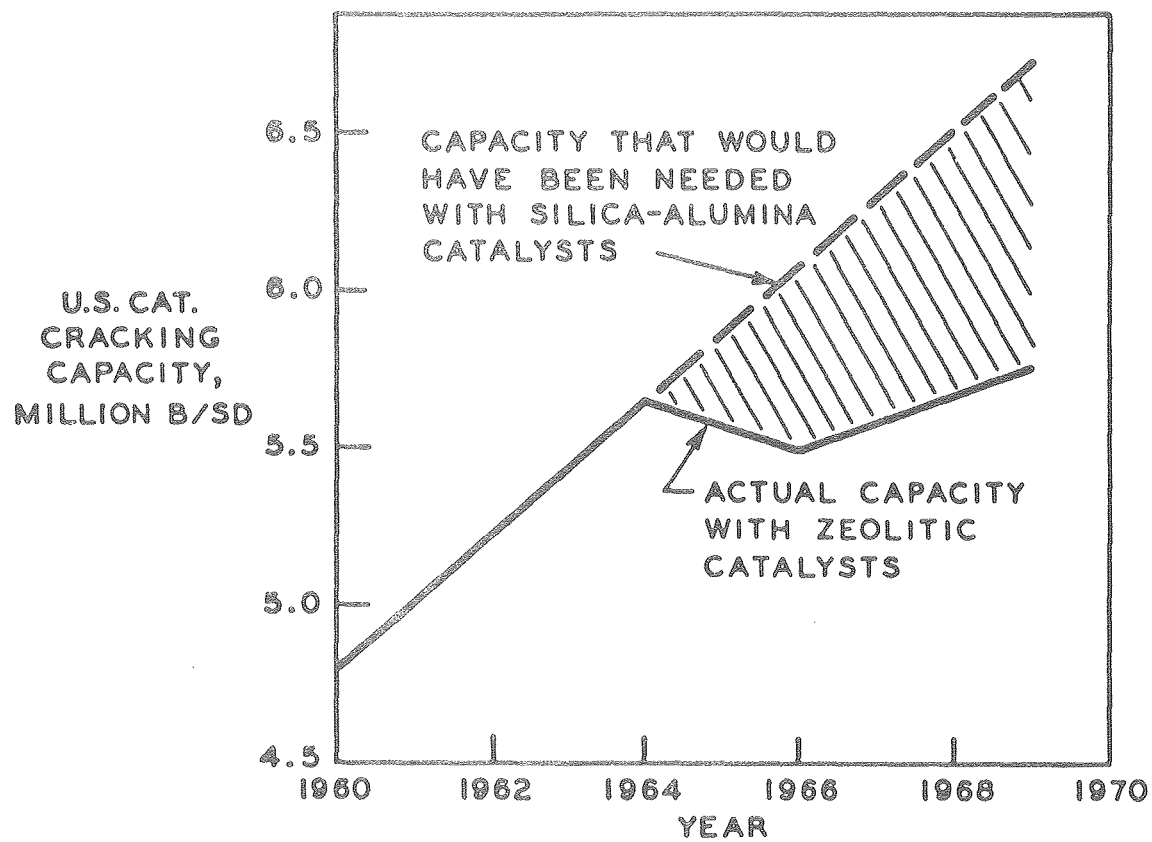


Fig. 7. Faujasite Zeolite

The new zeolite-cracking catalysts exhibited greater activity and selectivity than all previous catalysts (Tables 2 and 3). While their initial introduction was for use in TCC units in late 1961, fluid-bed zeolite catalysts were soon manufactured and used. The great selectivity of these catalysts sharply reduced the amount of gas oil required to produce gasoline. Figure 8 shows the U.S. catalytic cracking capacity as a function of time. The sudden change of slope in the years between 1964 and 1970 is due to the fact that the capacity of existing units was increased by the use of zeolite catalysts to such an extent that the steadily increasing demand for gasoline could be met for several years without new capacity. It has been estimated that savings of crude oil alone by this improved selectivity amounted to about \$200 million per year, prior to the quadrupling of oil prices in 1974. No history of industrial catalysis would be complete without mention of the patent litigation that ensued for more than ten years and ended with upholding the validity of the Plank and Rosinsky patents. About 90 percent of all catalytic cracking today employs zeolite catalysts. About 290 million pounds of cracking catalyst with a value of \$145 million were produced in 1978. ⁽¹⁷⁾

A series of catalyst improvements followed the initial introduction of zeolites, each adding to stability or selectivity of the catalyst. ⁽¹⁸⁾ In 1977, a new series of catalysts came on the market which contained, in addition to the zeolite, a combustion promoter. This permitted catalyst regeneration to very low residual coke levels at relatively low regeneration temperatures, and also permitted oxidation of CO to CO₂, reducing pollution and heat-loss problems. These catalysts, again developed by Mobil Oil, contain extremely small amounts (0.01-50 ppm) of platinum impregnated on the catalyst or introduced with the feed stock. ⁽¹⁷⁾ The role of oxidation promoters was well-known. But many previous attempts to incorporate them into cracking catalysts failed, because the oxidation component

EFFECT OF ZEOLITIC CATALYSTS ON CATALYTIC CRACKING CAPACITY



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Figure 8

Table 2⁽¹⁵⁾

Comparison of Gasoline Compositions from Gas Oil
Cracking Catalysed by Silica-Alumina
and Zeolite

Feed:	Calif.virgin gas-oil		Calif.coker gas-oil		Gachsaran gas-oil	
Catalyst, durabead gasoline	5	1	5	1	5	1
% Paraffins	21.0	8.7	21.8	12.0	31.9	21.2
% Cycloparaffins	19.3	10.4	13.4	9.5	14.3	15.7
% Olefins	14.6	43.7	19.0	42.8	16.3	30.2
% Aromatics	45.0	37.3	45.9	35.8	37.4	33.1

Durabead 1 = silica-alumina

Durabead 5 = early generation zeolite (REHX)

Table 3⁽¹⁵⁾

Yields of Products from Cycle Stocks Cracked Over
Durabead 5 and Durabead 7 Compared with Si/Al

	Si/Al Yields	Durabead 5 ¹ Yields	Delta Si/Al	Durabead 7 ² Yields	Delta Si/Al
Augusta catalytic light fuel oil ³					
Conversion, Vol %	35.6	35.6	-	35.6	-
C ₅ + gasoline, Vol %	22.1	25.9	+3.8	29.2	+7.1
Total C ₄ 's, Vol %	8.7	7.9	-0.8	6.2	-2.5
Dry gas, Wt %	5.2	4.1	-1.1	3.5	-1.8
Coke, Wt %	4.3	2.2	-2.1	1.4	-2.9
Beaumont heavy catalytic fuel oil ⁴					
Conversion, Vol %	42.5	42.5	-	42.5	-
C ₅ + gasoline, Vol %	24.5	26.3	+1.8	30.6	+6.1
Total C ₄ 's, Vol %	9.4	9.4	0	8.2	-1.2
Dry gas, Wt %	6.5	5.2	-1.0	4.7	-1.5
Coke, Wt T	8.7	7.8	-0.9	4.9	-3.8

¹Contains REHX in silica-alumina.

²Contains REHY in silica-alumina.

³Properties—27.3°API, Aniline No. = 139.5°F, (59.8°C), ASTM boiling range = 516°-666°F. (269-353°C).

⁴Properties—19.5°API, Aniline No. = 157.5°F, (69.8°C) ASTM boiling range = 410°-760°F. (210-405°C).

acted also as a dehydrogenation component during cracking, and resulted in undesirably large yields of hydrogen. No such effect has been observed with the new catalysts. One must marvel, however, at the turnover rates these tiny amounts of precious metal must achieve during regeneration. It raises the old question of how much of the surface of catalysts is active in a catalytic reaction.

The introduction of a zeolite-cracking component into hydrocracking catalysts will be discussed in the section on dual functional catalysis.⁽¹⁰⁾ This was commercialized by Chevron and Union Oil Company of California about 1970.

Almost simultaneously with the introduction of zeolite-cracking catalysts came the discovery of catalytic shape selectivity by P. B. Weisz and his co-workers at Mobil.⁽¹⁹⁾ They stipulated and demonstrated that diffusional constraints prevented the entry of molecules above certain dimensions into the pores of certain zeolites, and introduced the concept of "molecular engineering." The first process based on this concept was disclosed in 1968 and was called "Selectoforming."⁽²⁰⁾ The catalyst used was a naturally occurring zeolite with about 5 \AA pore openings (contrasting the 9-12 \AA openings of faujasites and the 3 \AA of zeolite A). When a catalytic reformat was passed over this catalyst containing a small amount of nickel as a hydrogenation component in the presence of hydrogen, a selective cracking of n-paraffins occurred while branched chain hydrocarbons and aromatics passed undisturbed. This resulted in the removal of the lowest octane number components of gasoline, converting them mostly to LPG hydrocarbons.

Since 1974, a series of novel processes was introduced by Mobil Oil based on the unique properties of a synthetic zeolite called ZSM-5.⁽²¹⁾ (Fig. 9). This material has pore openings of 5-7 \AA and exhibits shape selectivity, acid activity, and an unusual resistance to coking. It extended the range of "Selectoforming" by cracking both normal and singly branched paraffins, but not the high-octane

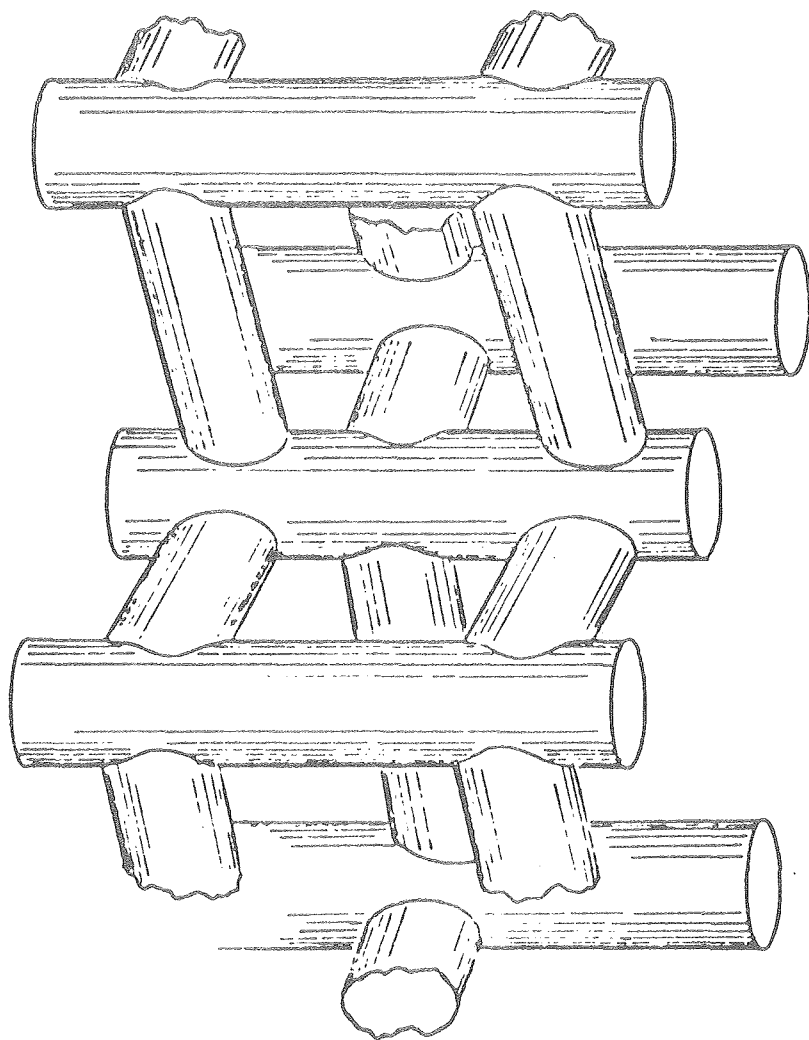


Fig. 9. Pore Arrangement of ZSM-5 Zeolite

number hydrocarbons possessing a quaternary C atom. In addition, it permitted simultaneous alkylation of simple aromatics like benzene with the olefinic fragments from paraffin cracking, resulting in higher liquid yields.⁽²²⁾ The "M-forming" process was first operated in Germany in 1976.

Shape selective cracking also is the basic reaction of the "Mobil Distillate Dewaxing" (MDDW) process.⁽²³⁾ This process was first tested in a commercial installation in France in 1974 and has been operating in a number of refineries in various parts of the world since 1978. It serves two purposes: one is lowering the pour point of middle distillate fractions such as diesel and heating oils to make them suitable for cold-weather operations, the other is permitting the inclusion of higher boiling material in these fractions to increase their yield-per-barrel of crude oil. In both cases, the pour point reduction is achieved by cracking waxy normal paraffins selectively with a relatively small yield loss. The cracked product consists largely of gasoline of good octane number. The reaction is carried out over ZSM-5-type zeolite in the presence of hydrogen, but there is essentially no hydrogen consumption. Catalyst deactivation is gradual and can be reversed by a hydrogen purge, indicating that it occurs probably by sorption of nitrogen compounds on the catalyst.

In another section (dual functional catalysis), mention will be made of xylene isomerization. ZSM-5-type catalysts have largely replaced $\text{Pt-Al}_2\text{O}_3$ in this application. They isomerize the three xylenes to equilibrium. Ethylbenzene is largely disproportionated eliminating the need for fractionation to remove ethylbenzene from the feed. Catalyst life in this application has exceeded two years. Recent patents indicate that chemical modification of ZSM-5 with phosphorous or carbon can further increase selectivity and result in p-xylene yields far exceeding equilibrium.

The same type of catalyst can replace AlCl_3 in the alkylation of benzene with ethylene to produce ethylbenzene.⁽²¹⁾ This eliminates catalyst disposal problems and substitutes a fixed-bed reactor system for a sparged tower.

Toluene disproportionation to benzene and xylenes is another commercial process operated with the ZSM-5 class of catalysts.

The latest application of this type of catalyst--which has not yet become commercial although it has been in operation in a sizeable pilot plant--is conversion of methanol to high-octane gasoline.⁽²⁴⁾ This new chemical reaction involves an internal dehydration and polymerization with simultaneous isomerization and hydrogen transfer. Methanol goes via dimethylether to an olefinic entity, which then forms isoparaffins and aromatics. The catalyst is ZSM-5 and operation can be in either fixed or fluid bed at quite mild conditions. The importance of the reaction lies in the possibility of converting either coal or natural gas via methanol (a well-established old technology) to gasoline. Several reaction mechanisms have been suggested for this reaction that had not been previously observed. It is not limited to methanol, but works with higher alcohols, ethers, and other oxygenates. The yields are stoichiometric, in the case of methanol giving 44 percent hydrocarbons and 56 percent water. The reaction is highly exothermic and heat removal is the major engineering process problem. Variations in operating conditions permit changes in the aromatics/paraffin ratio, and allow relatively high yields of ethylene and propylene.

IV DUAL FUNCTIONAL CATALYSISa) Naphtha Reforming

Catalytic reforming of naphthas serves to improve the octane number of gasoline by isomerizing paraffins, dehydrogenating cyclohexanes, dehydroisomerizing methylcyclopentanes, aromatizing some paraffins and also hydrocracking some paraffins.

The reforming of straight-run naphthas to achieve production of high-octane number gasolines developed slowly from thermal reforming^(25) to conversion over molybdena-alumina catalysts at elevated pressures

and in the presence of hydrogen. This process was used during World War II to produce toluene from methylcyclohexane. A continuous fluid bed process commercialized by Standard Oil of Indiana never achieved broad application after an explosion destroyed the first commercial plant in 1947, demonstrating the hazards of operating high-pressure hydrogenative processes in a continuous mode. About 1950 a new generation of reforming processes were introduced. "Platforming," the most successful of them, was developed by Universal Oil Products Company (UOP) and was also first on the market, closely followed by "Catforming" (Atlantic Refining Company) and "Houdriforming" (Houdry Process Corporation). All three processes employed a platinum catalyst on an acidic base. In "Platforming" and "Houdriforming," 0.3-0.8% Pt was supported on γ -alumina, and high activity levels were maintained by adding very small amounts of a hydrogen halide or hydrogen halide precursor to the feed. In "Catforming," the catalyst support consisted of a silica-alumina gel. All three processes operated at 400-600 psig (27-40 at) in the presence of hydrogen, and at 800-950 °F. (430-510°C) Life cycles were long and activity was maintained by gradually raising the temperature of operation to balance catalyst deactivation. After six to twelve months of operation, the catalyst was replaced by a fresh batch and the platinum of the spent catalyst was recovered by solution chemistry. Somewhat later it was learned that these catalysts could be regenerated by careful oxidation. The major improvements achieved by these catalysts were the ability to isomerize paraffins to highly branched entities, dehydrogenate naphthenes to aromatics, dehydroisomerize methylcyclopentanes to aromatics, and convert some paraffins to aromatics by dehydrocyclization. In the course of naphtha reforming, hydrogen is produced as another product, and this reformer hydrogen supplies a large percentage of refinery demand for hydrogen. The dual functional nature of reforming catalysts, possessing hydrogenative-dehydrogenative function as well as acidic properties, was described in 1953 by Mills, Heinemann, Milliken, and Oblad⁽²⁶⁾ and is illustrated in Figure 10.

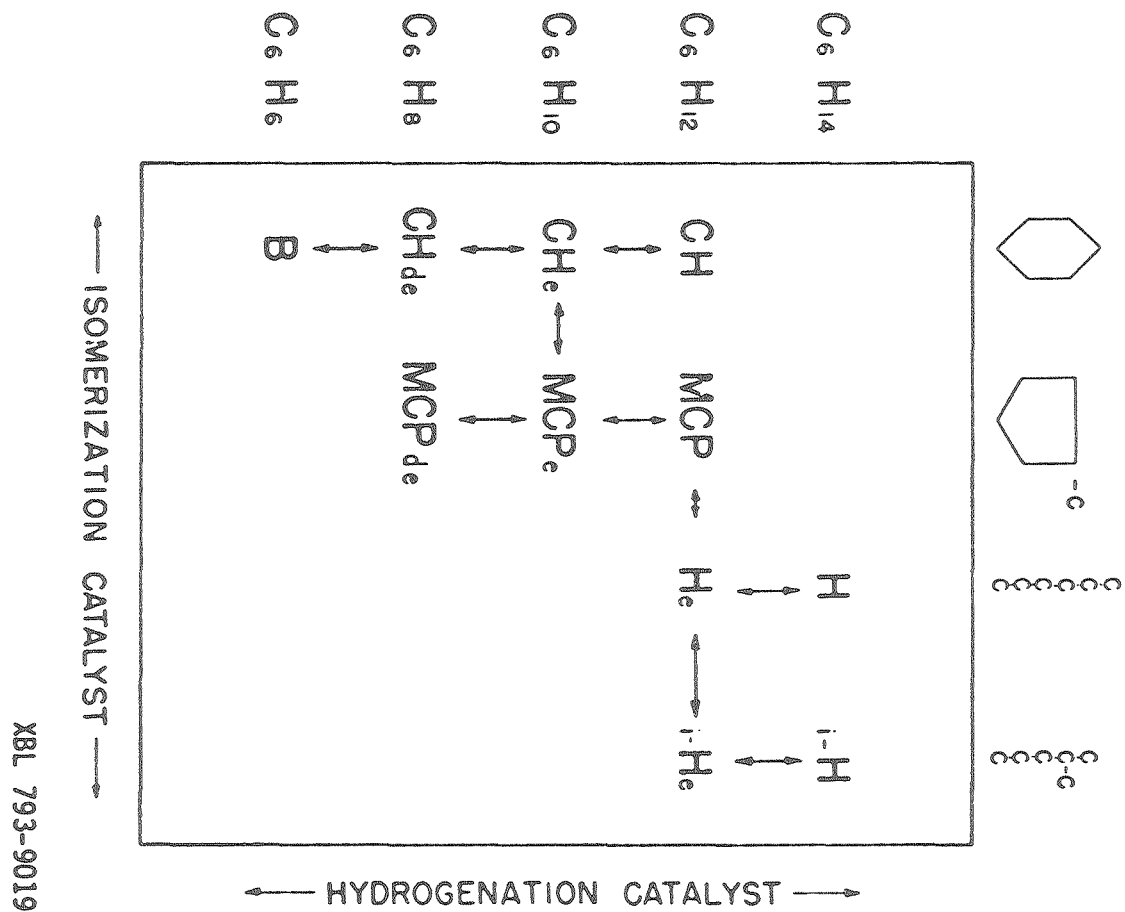


Fig.10. Dual Functional Reforming
Figure taken from reference 26.

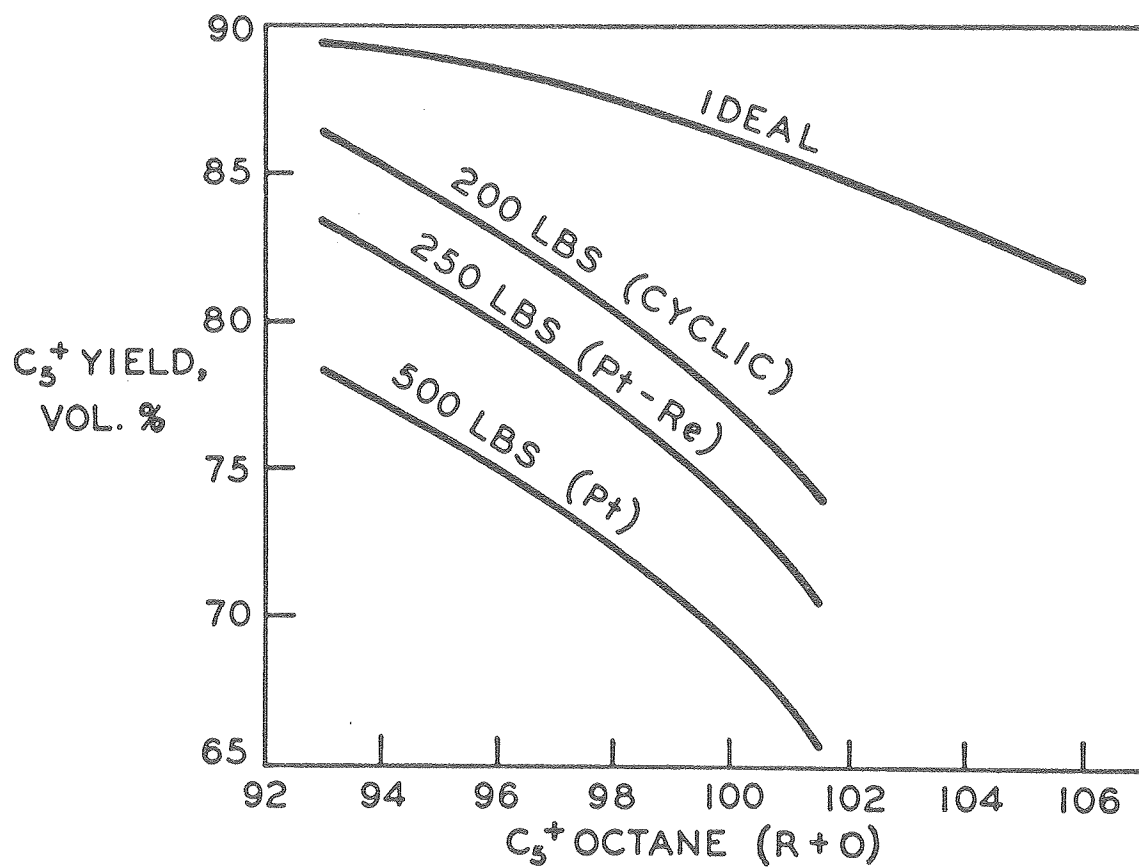
Their stipulation of the intermediary role of olefinic entities in the reaction mechanism was confirmed by P. B. Weisz and C. D. Prater in 1956, ⁽²⁷⁾ who showed the presence of these olefins in the small amounts permitted by equilibrium considerations.

Since aromatics have very high octane numbers (> 100) and can be tolerated in gasoline up to almost 50vol%, it was soon recognized that a high degree of aromatization was desirable and would proceed best at lower pressures. Figure 11 indicates the yield at various octane numbers at different pressures. Since catalyst deactivation increases as pressure is lowered, utilization of this concept required more stable and regenerative catalysts. It was found in 1953 that η -alumina was a more stable and active base; and in 1954 Standard Oil of Indiana introduced "Ultraforming," followed in 1956 by Esso's "Powerforming." These latter processes employ a cyclic mode of regeneration. Because of the relative ease of regeneration, the reforming can be operated at lower pressures; this permits better aromatization and higher octane number at the expense of more rapid catalyst deactivation.

All reforming processes use a multireactor system (usually three reactors, see Figure 12. ⁽²⁸⁾ The first two reactors are endothermic because the major reaction in these is dehydrogenation; and the third reactor is exothermic because of hydrocracking and hydrogenation. Interstage heaters are employed to permit the same temperature at each reactor inlet. The last reactor operates at the highest average temperature and shows the most rapid aging. In the cyclic processes there is a spare reactor which undergoes regeneration, after which it is substituted for the first reactor, which becomes Number 2. The second reactor becomes Number 3, and the third is withdrawn and regenerated.

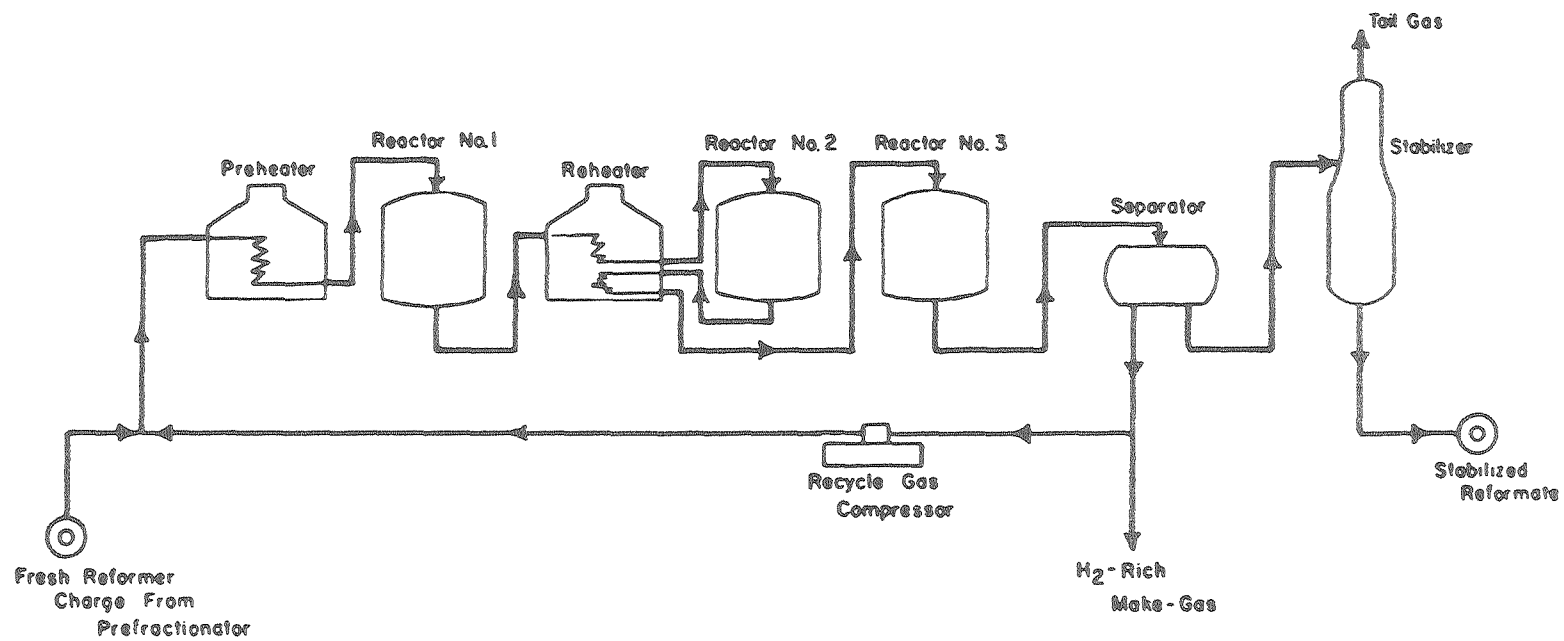
In the case of naphtha reforming, just as in catalytic cracking, the original process development involved the engineering design of a new unit concept as well as catalyst development.

YIELD VS. OCTANE FOR REFORMING
OF C₆-360 MID-CONTINENT NAPHTHA



XBL 793-9017

Figure 11



XBL 793-8901

Fig. 12. Catalytic Reforming Unit

In both cracking and reforming, further impressive improvements were achieved by catalyst modifications that permitted use of the new catalysts in existing units. In a period of high investment-and-construction costs, this reduced the risk of introducing new process technology--a risk that might otherwise have been unacceptable. A major step forward in the art of naphtha reforming occurred in 1967 with the introduction of catalysts containing, in addition to platinum, another metal (or metal oxide) on an alumina base. Chevron's "Rheniforming" process⁽²⁹⁾ was first on the market. This catalyst, containing rhenium in addition to platinum, provides greater stability. In 1975 Exxon commercialized operation with another catalyst, said to contain iridium and platinum and providing stable operation at quite low pressure. Sulfur sensitivity is greater than that for Pt catalysts. About 5 million pounds of reforming catalysts worth \$28 million were sold in 1978.⁽¹⁷⁾

Bimetallic catalysis is based on research on the concept of bimetallic cluster catalysts. Such catalysts consist of metallic clusters composed of atoms of two or more different metals in a state of high dispersion on a carrier.⁽³⁰⁾ The impact of this research, while already apparent in catalytic reforming as outlined above, is likely to increase over the next few years. Isomerization, hydrocracking, and hydrogenation will be affected. Vinylacetate manufacture with palladium-gold catalysts,⁽³¹⁾ and olefin partial oxidation (see section on oxidation) with silver-gold or copper-gold catalysts,⁽³²⁾ are in the offing.

b) Isomerization

Catalysts used for isomerization are almost identical with those used in reforming. This is natural since isomerization is one of the important functions of reforming. Of the several processes developed, the Shell and UOP C₅ isomerization processes have, since

the late 1950s, replaced AlCl_3 catalysis. In the case of aromatics isomerization, one is primarily concerned with xylene isomerization. In this case, p-xylene is removed (e.g., by fractional crystallization) from a mixture of xylenes. The remaining o- and m-xylene rich mixture is isomerized to equilibrium and the p-xylene again removed, recycling the remainder. Atlantic Refining Company's "Octafining" process using $\text{Pt-Al}_2\text{O}_3$ or $\text{Pt-SiO}_2\text{-Al}_2\text{O}_3$ catalyst was introduced in 1960 by Mitsui and has found broad application as p-xylene demand for dacron fabrics mushroomed. ⁽³³⁾ It operates in the presence of hydrogen at about 400-500 °F (205-260 °C) and 150-350 psig, (10-23 at) and the catalytic mechanism is similar to the one involved in reforming. Imperial Chemical Industries (ICI) has commercialized another process that employs silica-alumina cracking catalysts at 400-500 °C and atmospheric pressure in the absence of hydrogen. This process requires frequent catalyst regeneration (every second or third day), while the "Octafining" process operates on the same catalyst charge for six to twelve months, without regeneration.

In 1976 Mobil Oil Corporation introduced the "Mobil Vapor Phase Isomerization Process" (MVPI) and in 1978 the "Mobil Low Pressure Isomerization Process" (MLPI), each employing zeolite catalysts. These have been discussed in the section on zeolites. The MVPI process has conquered about three-fourths of the free-world's C_8 isomerization capacity. It is not a dual functional catalyst, nor is the ICI catalyst.

c) Hydrocracking

Hydrocracking has assumed increasing importance as feedstocks for fuels became heavier and supplies of gas oil for catalytic cracking and of naphtha for reforming became insufficient to supply the gasoline market. The relatively high carbon/hydrogen ratio of high-boiling fuels and their aromaticity made them unsuitable as cracking feedstocks, at least without prior hydrogenation. Conversion of heavier gas oils by hydrogenative processing dates back to pre-World War II technology

developed by M. Pier and his associates at I.G. Farben Industrie in Germany between 1925 and 1930, in collaboration with Standard Oil of New Jersey, operating at pressures of 3000-5000 psig. (200-333 at). The combination of hydrogenative and acid functions in catalysts to convert heavy petroleum fractions to gasoline and dry gas under high hydrogen partial pressure, however, did not become a large-scale commercial reality until the 1960s. This was primarily because long catalyst life was required for a process operating at high pressure (with the time-consuming and costly requirement to depressure, purge, and after regeneration to purge and repressure again), and also because nitrogen compounds in the feed tended to rapidly deactivate the cracking function. About 1960, catalysts and systems were found that operated at lower pressures (2000 psig).

Union Oil Company (together with Esso) and Chevron Oil Company pioneered hydrocracking processes using nickel or nickel-tungsten on silica-alumina as catalysts. (34) In later versions, zeolites of the fanjasite type were substituted for the silica-alumina base in about 1966-1967. With feeds having high nitrogen compound content, a two-reactor system was used in which the nitrogen compounds were converted in a first hydrogenation reactor to ammonia over nickel-tungsten or tungsten sulfide on alumina or silica with, of course, concomitant hydrogenation of some aromatics. Ammonia at high hydrogen partial pressure is less of a poison to acid catalysts than organic nitrogen and would be tolerated in the second hydrocracking reactor. In one version of the process, separate hydrogen circulation systems are used for the two reactors, with an acid wash to remove ammonia and a carbonate wash to remove H_2S from the hydrogen cycle.

Hydrocracking has become an integral part of refinery operations, with a U.S. capacity of about 900,000 bbl/d, but has lately encountered competition from hydrogenation (see section on metallic and multimetallic catalysis) and subsequent catalytic cracking, and capacity has remained fairly constant during the last five years.

V HYDROGENATION CATALYSIS AND HYDROGEN PRODUCTION

One of the oldest of catalytic reactions is the saturation of fats over nickel catalysts. In general, metallic catalysts have found their most widespread use in the activation of the hydrogen molecule.

a) Desulfurization and Denitrification

The greatest new industrial uses during the last 30 years have again occurred in the petroleum industry. With increasing supply of high-sulfur crude oils and the need to remove sulfur and nitrogen compounds for pollution abatement as well as to produce streams that can be subsequently treated over sulfur or nitrogen sensitive catalysts (e.g., in catalytic reforming, methanation, or hydrocracking), large hydrogenation units have been built, mostly to convert organic sulfur and nitrogen compounds to H_2S and NH_3 , respectively, which in turn can then be removed by washes or adsorption. The most common catalysts used are cobalt-molybdena on alumina, molybdenum sulfide on alumina, and tungsten and/or nickel sulfide on supports. For the desulfurization of distillates, the operation is carried out at 500-700 psig (33-47 at) Pressure and temperatures of 600-800°F, (315-430°C) space velocities of 1-5 v/v/hr. The catalyst can be regenerated periodically by air burning, and catalyst life between regenerations is long--usually more than six months. This technology is derived from old German work of the 1930s, but found general use only in the 1950s.

More recently--in the late 1960s and early '70s--desulfurization of residual materials became important. This is more difficult, and catalyst poisoning is irreversible because of the deposition of heavy metals (V, Ni, Fe) from the oil on the catalyst. Conditions of this type of operation, pioneered largely by Gulf Oil and Esso, are more severe; pressures range up to 2000 psig (130 at) and space velocities are as low as 0.3 v/v/hr. It was found by workers that the pore

characteristics of the catalyst support are of great importance. Large pores are required to allow some of the very large carbon molecules containing hetero atoms to diffuse into the catalyst, while small pores are needed to provide the overall high surface area. (35) The technology has developed in two directions: 1) Catalysts with a very wide pore distribution have been used, ranging from 10\AA to 1000\AA ; 2) Catalyst beds have been graded with large pore catalysts first contacting the oil, and a decreasing pore-size catalyst treating partially converted feed. Hydrosulfurization and hydrodenitrogenation catalysts are not selective to S and N compounds, and in all operations saturation of aromatics occurs as a side reaction, using up much more than the stoichiometric amounts of hydrogen required to convert sulfur or nitrogen compounds.

b) Selective Hydrogenation

Since 1975, considerable thought has been given to the hydrogenation of recycle stocks. These highly aromatic fractions from the catalytic cracking of heavy gas oils can be saturated, essentially in the type of operation described above, and are then suitable as catalytic cracking feeds. In many cases, this eliminates the need for hydrocracking.

Another application of hydrogenation is a selective one. In the steam cracking of ethane or naphtha to produce ethylene and propylene, a byproduct called pyrolysis gasoline is obtained which contains aromatics (benzene, toluene, xylenes) as well as olefins and diolefins. Before the aromatics can be extracted, it is necessary to saturate the olefins and diolefins without saturating the aromatics. Several commercial plants were built in the period between 1955 and 1965 using mostly nickel-sulfide catalysts for this treatment at relatively mild conditions. In a variant of the process, only the diolefins are saturated and the aromatic-olefinic product is blended as a high-octane component into gasoline.

Olefins produced from naphtha by steam cracking usually contain small but bothersome amounts of diolefins and acetylenes, such as butadiene, isoprene, and methylacetylene. These must be removed prior to polymerization of the olefins. This is usually done by selective hydrogenation over supported palladium catalysts under conditions that will not cause hydrogenation of mono-olefins.⁽³⁶⁾ Operating conditions are 35-100 °C and 3-30 atm. pressure. Nickel-cobalt-chromium catalysts have also been used for this purpose. In 1963, Farbenfabriken Bayer announced a liquid-phase selective hydrogenation process using a palladium catalyst which operates at very low temperatures. This has since been commercialized.

c) Hydrogen Production

Hydrogen for hydrogenation reactions comes mostly from two sources: reformer hydrogen, and the product from the steam-hydrocarbon (or steam-carbon) reaction. The steam-hydrocarbon reaction is called "steam reforming." It produces "synthesis gas," a mixture of hydrogen and carbon monoxide. The carbon monoxide is reacted over a water-gas shift catalyst with water to form more hydrogen and carbon dioxide, which can be scrubbed from the gas mixture leaving relatively pure hydrogen.

Hydrogen as a by-product from naphtha reforming has already been mentioned in the section on Dual Functional Catalysis. Production of hydrogen by steam reforming from methane, naphtha, heavy oil, and coal has achieved increasing importance in recent years. This is because of the increased demand for hydrogen, both for petroleum refining processes such as hydrotreating and hydrocracking, and for petrochemical use in the production of ammonia and methanol, among others. Steam reforming has recently been reviewed.⁽³⁷⁾

While the reaction between carbonaceous material or hydrocarbons and steam over catalysts such as nickel on supports has long been known and used, a major breakthrough was achieved in 1962.⁽³⁸⁾

Until then, the reaction of hydrocarbons and steam was limited to relatively low pressures. The reason for this is that, in addition to the reaction $C + H_2O = CO + H_2$ and similar reactions for hydrocarbons, there is also a decomposition of hydrocarbons to produce carbon and hydrogen. The deposition of carbon on the catalyst rapidly deactivates the catalyst. At increasing pressures, this decomposition becomes faster at the temperatures involved than the reaction of steam and water. It was therefore necessary to accelerate the carbon-steam reaction so that it equaled or became faster than the hydrocarbon decomposition. This was achieved almost simultaneously by the M. W. Kellogg Company in the United States and the Imperial Chemical Industries (ICI) in Great Britain.⁽³⁹⁾ It was found that the carbon-steam reaction could be greatly accelerated by the presence of alkali or earth-alkali ions, and that catalysts containing sodium or potassium oxide in addition to the customary nickel⁽³⁸⁾ could perform at relatively high pressures up to 500 or 600 psig. (33 or 40 at) without this discovery, the new generation of ammonia plants (see following paragraphs) which operate at pressures of about 2000 psig (133 at) would not have been possible. By using a liquid feed such as naphtha or heavier hydrocarbons at pressures up to 500 pounds (33 at) which can be achieved by pumps, the remaining pressure difference of about 1500 psig (100 at) can be obtained by a single-stage compressor. The discovery of alkali promoted nickel catalysts for the steam-carbon reaction made possible a revolution in the ammonia industry and the creation of large-scale plants to produce ammonia at about one-half the cost of older generation plants. Alkali catalysts will also be important for the production of hydrogen and of methane from coal or char and water.

As already mentioned, if the production of hydrogen alone rather than synthesis gas is desired, it is necessary to react carbon monoxide with water to produce CO_2 and hydrogen.⁽⁴⁰⁾ The exothermic water-gas shift process is used at 310-490 °C with an excess of water vapor; chromia-iron oxide catalysts are used with many improvements

in detailed catalyst composition having occurred during the past 20 years. Copper oxide-zinc oxide-alumina catalysts have also found application. Shift catalysts are available from several catalyst manufacturers.

d) Ammonia Synthesis

The synthesis of ammonia ($N_2 + 3H_2 \rightarrow 2NH_3$) was discovered in the early part of the 20th century and has been widely described. The first plant was built in 1913 by BASF in Germany. While improvements have been made in the catalyst used, ⁽⁴¹⁾ these are of relatively minor importance and can be neglected in a history of industrial catalysis. Most catalysts are based on magnetite containing some alumina and CaO with alkali promoters. A major breakthrough, however, was achieved in the late 1950s when it became possible to build very large (1000 tons per day plus) ammonia plants of a simplified nature, and with greatly reduced investment and operating costs. The resultant reduction in the cost of ammonia increased the demand for ammonia as a fertilizer and has greatly contributed to avoiding famine in many parts of the world. This breakthrough is based on a combination of chemical and mechanical inventions. The chemical part of this invention, namely the production of hydrogen at relatively high pressures, has been detailed in a previous paragraph; the mechanical part of the invention consists of the introduction of single-train large units with one-stage centrifugal compressors rather than two or more stages of reciprocal compressors. Operation is being carried out at somewhat lower pressures than previously used (current operating pressures are in the order of 2000 psig (133 at)), even though equilibrium conditions are somewhat less favorable there than at higher pressure. However, this is greatly overcome by savings in operating and utility costs. Other mechanical improvements in ammonia synthesis include new reactor designs that permit greater efficiency. The first company to introduce the new design of ammonia plants was M. W. Kellogg.

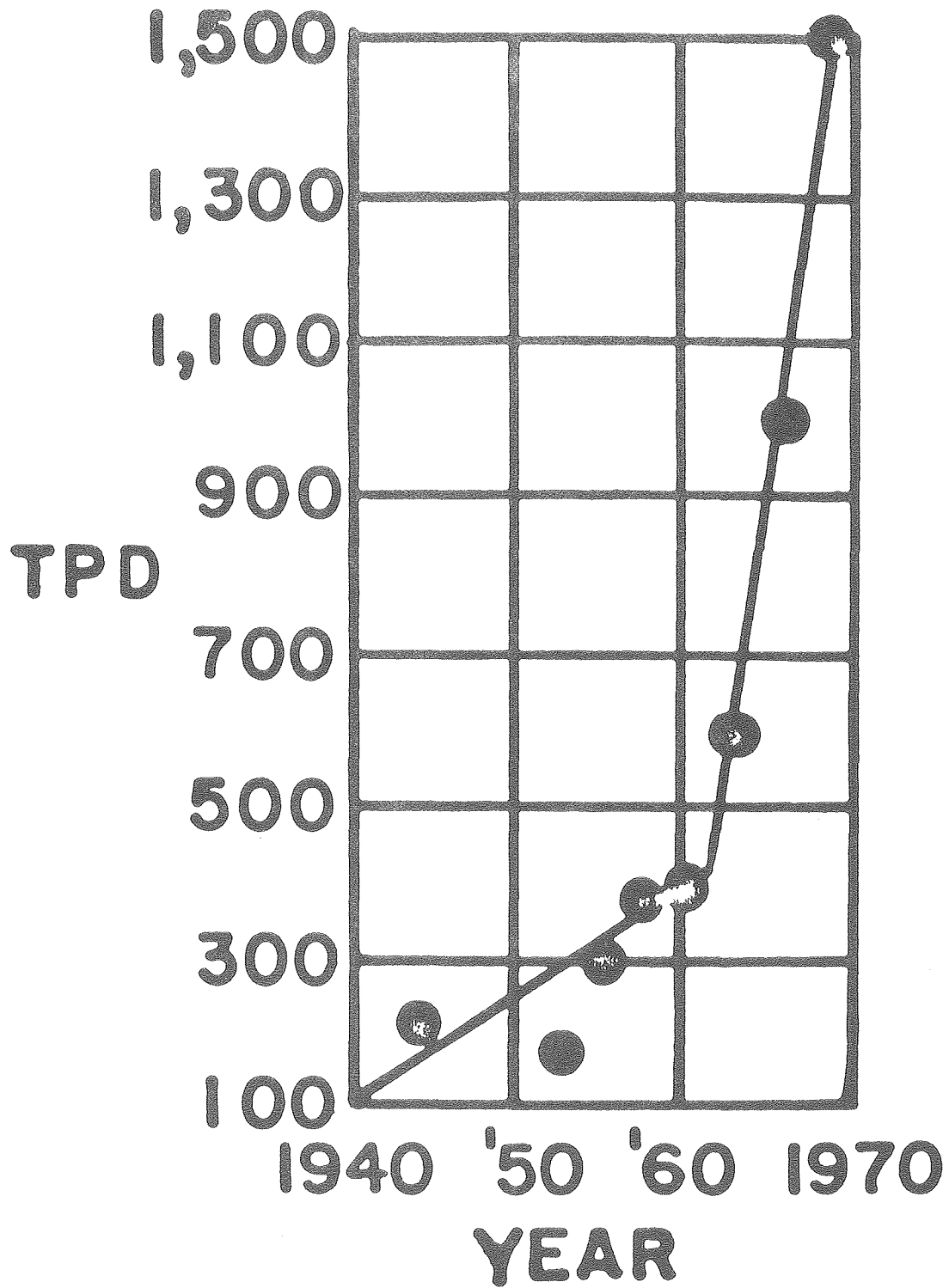
Increased demand for ammonia as a result of these improvements is shown in Figure 13, which presents the size of individual plants as a function of time, and illustrates the rapid increase in capacity after the new generation of plants came into existence.

e) Methanol Synthesis ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$)

The synthesis of ammonia and of methanol parallel each other in many ways. In fact, the unit design for the two processes is almost identical. Like ammonia, methanol synthesis dates back many years (it was commercialized in 1924). Mechanical improvements parallel those of ammonia synthesis. Chemical improvements were achieved around 1966 by Imperial Chemical Industries' discovery of a low-pressure methanol catalyst. This catalyst is comprised of zinc, copper, and alumina and permits operation at significantly less pressure (750 psig (50 at) vs. 2000 psig (133 at)) and lower temperature than the old historic zinc-alumina-chromia catalyst allowed, and has therefore contributed to a more economical production of methanol. (42) The advantages of a high-pressure production of synthesis gas as outlined above are applicable to the methanol synthesis as they are to the ammonia synthesis.

In addition to new catalyst developments, there have also been new reactor designs for methanol synthesis. The Lurgi reactor consists of a large number of relatively small-diameter catalyst-containing tubes. A bundle of these tubes is surrounded by a jacket filled with pressurized water. Control of the steam pressure in the jacket controls the temperature of the water, and provides an excellent heat-exchange medium for the exothermic methanol synthesis reaction.

These developments in ammonia and methanol syntheses are a clear demonstration of the fact that even technologies considered mature can undergo revolutionary developments that will change the demand-and-supply picture because of greatly reduced product prices.



XBL 793-9018

Fig. 13. Capacity of Individual
Ammonia Units Built

VI CATALATIC HYDROCARBON DEHYDROGENATION

Commercial dehydrogenation processes relate essentially to two types of operation involving different catalysts: 1) butane dehydrogenation to butenes and/or butadiene, 2) ethylbenzene dehydrogenation to styrene monomer.

Butane dehydrogenation was pioneered by Eugene J. Houdry and Houdry Process Corporation during World War II and has been reviewed in detail. (43) It is carried out to yield either butenes or butadiene, or both. Chromia-alumina is the preferred catalyst for this reaction. The catalyst is easily deactivated by steam, the presence of which during reaction must be avoided. Improvements made since installation of the first commercial plants in the mid-1940s are mostly of a mechanical nature and relate to operational time and conditions, and to catalyst regeneration time. Since the reaction is highly endothermic, heat generation for maintaining reaction temperature is dependent on burning coke deposits on the catalyst. A fine balance is required between coke lay-down and regeneration and operating time.

Oxidative dehydrogenation of butanes or butenes to butadiene is practiced over bismuth molybdate catalysts at 400-500°C. The exothermicity of oxidation supplies most of the heat requirements of the endothermic dehydrogenation. The impetus for commercial production of styrene in the United States lay in the critical need for a substitute for natural rubber during World War II. As a result of an industry-wide cooperative effort, an annual production capacity of over 400 (180) million pounds (Kg) was installed in only two years. This effort has been surveyed by Boundy and Boyer. (44) The best catalysts, still in use after more than 30 years, are comprised of alkali-promoted iron oxide and the reaction is carried out in the presence of steam to reduce hydrocarbon partial pressure. The best catalysts are unsupported. The major by-products from the dehydrogenation are benzene and toluene. A discussion of the effect of promoters on iron oxide can be found in E. H. Lee's review. (45)

VII CATALYTIC DEALKYLATION

Hydro dealkylation is a process used for the production of benzene from toluene. Thermal as well as catalytic processes have been developed. Demethylation must be selective and hydrogenation of the aromatic ring must be avoided. High purity, low sodium chromia-alumina catalysts are used at 550-650°C and 35-80 at pressure (12). Because of the exothermicity of the reaction, close temperature control is required.

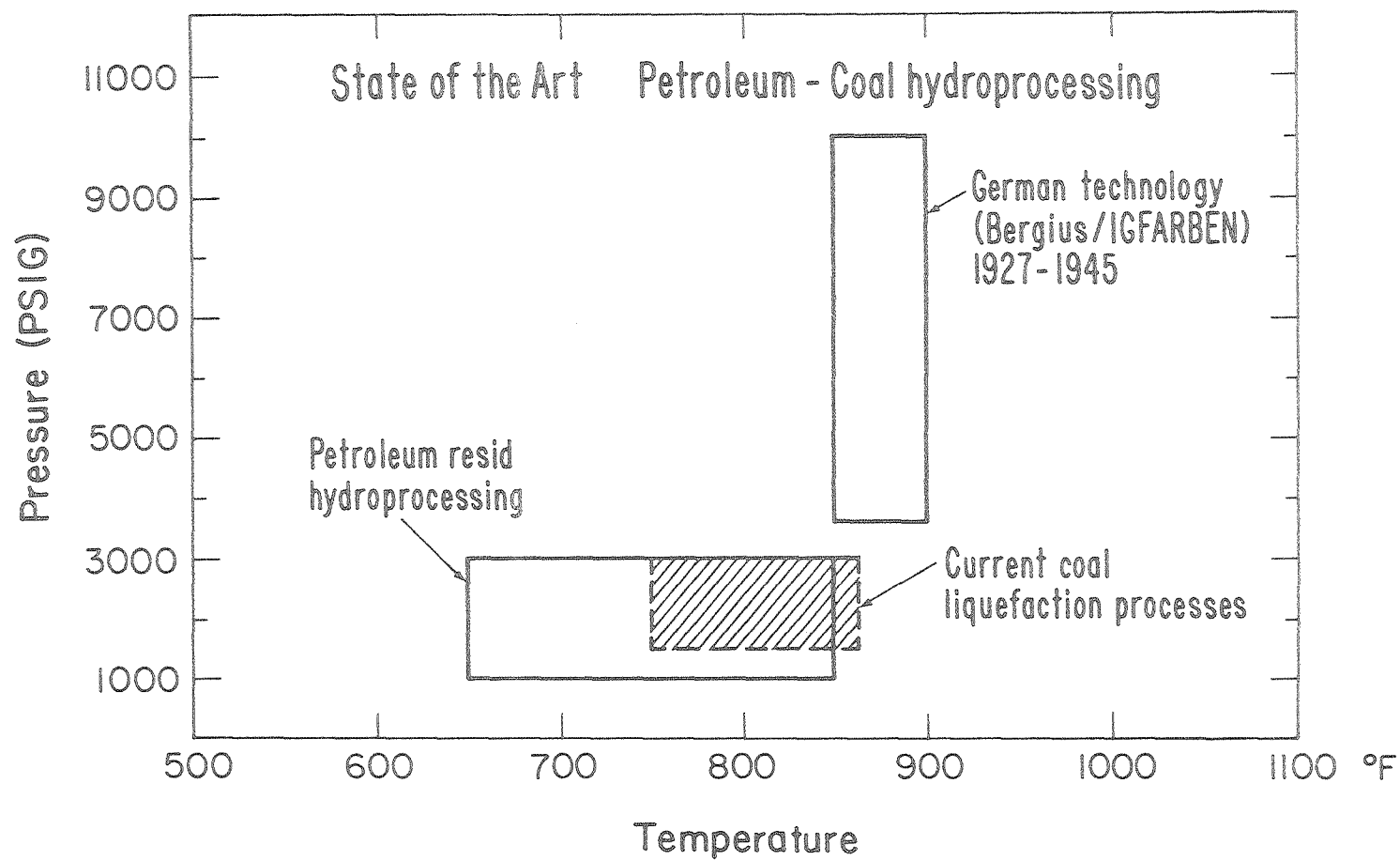
VIII CATALYTIC COAL LIQUEFACTION AND GASIFICATION

a) Liquefaction

Production of liquid fuels from coal is based on two technologies discovered in Germany in the 1920s: the Bergius process for direct catalytic hydrogenation in a solvent, and the Fischer-Tropsch process involving the reaction of coal and steam to produce synthesis gas ($\text{CO} + \text{H}_2$) and subsequent hydrocarbon synthesis from this gas. Both technologies have been repeatedly reviewed. (46; 47; 48)

Both processes found large-scale commercial application in Germany during World War II, and a Fischer-Tropsch plant was built in South Africa in the mid-1940s and has been operating since, with a second larger facility to start operating in 1981, and a third one announced in 1979. While there was much active research on both the direct (hydrogenation) and the indirect (Fischer-Tropsch) liquefaction routes in the United States and in England during the 1940s and early '50s, interest lapsed when large volumes of inexpensive petroleum was discovered in the Middle East. Not until the 1970s was research intensified again, especially after the Arab oil embargo of 1974. No new commercial facilities other than the South African SASOL plant have been built as yet, but several new processes are being developed.

The new direct-hydrogenation processes are directed toward operating at lower-pressure and lower-hydrogen consumption than the Bergius process, as shown in Figure 14. Two of the three major processes being developed employ catalysts. In the H-coal process, the coal is dissolved in a recycle solvent containing largely aromatic and hydroaromatic hydrocarbons, and the resulting solution and/or slurry is contacted with a cobalt-molybdena alumina catalyst in an ebullating bed reactor. Catalyst life is said to be about one pound (0.5Kg) per ton of coal charged, or per 3 bbl of product. The operation is carried out at pressures in the range of 2000-3000 psig (133-200 at) and at temperatures of 750-850 °F. (400-450°C). After separation of the ash, products are fractionated and the solvent is recycled. Depending upon the



XBL 794-1052

Figure 14

Figure courtesy R. H. Fischer
U. S. Department of Energy

severity of the operation, the process operates in either a "syn-crude" or "fuel oil" mode. Hydrogen consumption is higher in the "syn-crude" mode (5000 cft/bbl) than in the "fuel oil" mode (3500 cft/bbl).

The "Exxon Donor Solvent" process distinguishes from the H-coal process by carrying out the hydrogenation by means of a donor solvent rich in hydroaromatics. This solvent is then rehydrogenated in a separate loop, using a conventional cobalt-molybdena catalyst. In this case, the catalyst is not subjected to potential poisons in the dissolved coal and slurried ash, and its life is therefore appreciably longer. The U. S. Department of Energy, jointly with industry, is currently sponsoring the erection and operation of large pilot plants for both processes.

The third major process (SRC) does not employ a catalytic reactor but it appears that the ash in coal possesses catalytic properties, which enhance thermal hydrogenation.

Indirect liquefaction also has been dormant until the mid-1970's, except for the SASOL plant. The major innovation at SASOL had been a fluid-bed operation of the synthesis reaction that permitted better temperature control and better yields of gasoline. H. Köelbel developed a liquid phase synthesis in a large pilot plant in Germany in 1948-1950.^(49;50) Conventional iron-type Fischer-Tropsch catalysts are suspended in a heavy oil. High-per-pass conversions (95%+) are obtained and it is possible to operate with relatively low hydrogen/CO ratios such as 0.6/1. Internal shift supplies the additional hydrogen required. The low H_2 /CO ratio could be of increasing importance as new and less expensive gasifiers supplying low H_2 /CO-ratio gas become commercial.

A new development announced in 1976 is the Mobil methanol-to-gasoline process (21) mentioned in the section on zeolites. This process, for which a large pilot plant is currently under construction, will provide a new route from coal to high-octane gasoline, and appears to be competitive with other coal liquefaction routes.

b) Gasification

In coal gasification there are two worthwhile developments. One involves the reaction of coal with steam in the presence of alkali carbonate. In the early and mid-1960's, the M. W. Kellogg Company did pilot plant work on a process in which coal dissolved in molten carbonate was reacted with steam to produce synthesis gas at high temperature and pressure.⁽⁵¹⁾ Sulfur compounds in the coal react with alkali carbonate to form hydrosulfides which can then be reconverted to carbonate under high CO_2 particle pressure. In 1977, Exxon announced work on a process to produce methane directly from coal and water at relatively low temperatures by impregnating the coal with 7-10 percent of alkali carbonate. Complete recovery of the alkali carbonate has not yet been demonstrated.

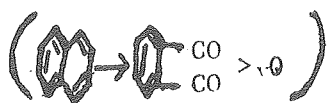
Many coal gasification plants are in operation and many new designs are being developed. None of these employs added catalysts and the catalytic role of coal ash in gasification, if any, is not well defined.

c) Methanation

Several methanation processes have been announced. The major catalytic step is the methanation of synthesis gas which takes place over a nickel catalyst. An interesting case is the use of a Raney nickel catalyst with which the reactor walls have been coated.⁽⁵²⁾ This is a novel technique and provides an alternative to supported nickel catalysts for the $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4$ reaction.

IX HETEROGENEOUS OXIDATION, AMMOXIDATION, CHLORINATION, AND OXYCHLORINATION CATALYSIS

a) Oxidation

Oxidation of naphthalene  over molybdena or vanadia catalysts is an old art used for many years for the production of phthalic anhydride. In 1946, Oronite Company (now Chevron) initiated the production of phthalic anhydride from o-xylene over vanadium oxide catalysts. The feed can be impure because other C_8 aromatics and paraffins are oxidized to CO_2 . Considerable progress was achieved

when the first fluid-bed oxidation plants for naphthalene or o-xylene charges were built in 1952-1953 by Imperial Chemical Industries and American Cyanamid Company. Since then, the Badger-Sherwin Williams fluid-bed process has found application in several large plants. The better temperature control of the fluid bed has permitted better selectivities. Similar processes are used for oxidation of benzene to maleic anhydride, and of toluene to benzoic acid.

The conversion of light hydrocarbons into products containing oxygen or other heteroatoms is of great importance to the chemical industry. Ethylene oxide and ethylene glycol, propylene oxide, acrolein, acrylic acid, and acrylonitrile are all large-volume chemicals that are produced today from ethylene or propylene by catalytic oxidation or ammoxidation, resp.

Ethylene oxide⁽⁵³⁾ is a very large-scale commercial product. Early attempts to oxidize ethylene directly to the oxide failed. In 1931, Lefort first reported success using silver as a catalyst. Union Carbide first commercialized a direct oxidation process in 1937; and Scientific Design Company and Shell Oil Company have licensed many installations since then. Silver is still the major active catalyst ingredient. Promoters are used with the silver, such as oxides of alkali and alkaline earths. Organic halides minimize the formation of CO₂. Ethylene oxidation processes are operated under recycle conditions in fixed-bed equipment at 250-325 °C and 10-50 atm. pressure. Conversion to ethylene oxide is about 70 percent, with much of the rest being lost to CO₂.

A new catalytic process for production of propylene oxide from propylene was commercialized by Oxirane Company in 1969.^(54; 69) Since it involves homogeneous catalysis, it is described in the section on Homogeneous Catalysis, as are other oxidation processes.

Hearne and Adams⁽⁵⁵⁾ described in 1948 the production of acrolein from propylene and oxygen $(C_3H_6 + O_2 \rightarrow CH_2=CH-CHO + H_2O)$ over cuprous-oxide catalysts. Yields were about 50 percent. Further improvements by Shell involved a copper-oxide/silicon-carbide catalyst promoted by iodine.

A most important discovery was patented in 1959 by Idol and in 1962 by Callahan,^(56; 57) who reported yields of acrolein much higher than those obtained in the old cuprous oxide system. The improvement was due to the selective action of a new type of catalyst--bismuth molybdate. Based on this discovery, Standard Oil Company of Ohio (SOHIO) commercialized vapor-phase propylene oxidation and ammoxidation processes.

b) Ammoxidation

Propylene, ammonia, and air are reacted in a fluid bed to give acrylonitrile and water ($C_3H_6 + NH_3 + 1\frac{1}{2}O_2 \rightarrow CH_2=CH-CN + 3H_2O$) Operation is at 400-500°C and 3-30 psig (0.2-2at) pressure. A once-through operation without recycle is feasible and the process has found worldwide application. Even more selective catalysts of the novel uranium antimonate system were disclosed in 1965, and in 1970 SOHIO introduced "multicomponent" catalysts containing several elements of the group consisting of nickel, cobalt, iron, bismuth, molybdenum, potassium, manganese, and silicon. Production of acrylonitrile by this type of catalysis was 2.5 million tons/yr in 1977.⁽¹⁷⁾

An alternative propylene oxidation route using tin plus antimony oxides as catalysts was also developed by SOHIO.^(54; 58)

A process which is somewhat related to ammoxidation involves the synthesis of methylpyridines from ammonia and acetaldehyde. It is carried out over silica-alumina catalysts, modified by thorium, zinc, or cadmium at 750-950 °F. (400-510°C) It gives yields of 40-60 percent.

c) Hydrohalogenation and Oxychlorination

Catalysts comprising inorganic metal chlorides have found application in hydrohalogenation reactions. Thus, bismuth and

antimony trichloride are used to add HCl to ethylene or propylene and mercuric chloride on carbon is a common catalyst for reacting acetylene with HCl to produce vinyl chloride.

Oxidation of HCl to chlorine over cupric chloride was first described by Deacon about 100 years ago. Attempts to operate a process on this reaction failed because of major corrosion problems. In 1969, M. W. Kellogg Company announced a successful process (which is discussed in the section on Homogeneous Catalysis).

In 1964, Goodrich, Dow, and Monsanto commercialized oxy-chlorination processes. (58; 59) Most of these are fixed- or fluid-bed operations over copper chloride catalysts, reacting ethylene and HCl and oxygen to dichloroethane and water. The copper salts are molten and sorbed in the alumina support at operating conditions; HCl produced in the direct chlorination of ethylene can thus be converted into the desired vinylchloride monomer. This development followed an earlier operation of the Raschig-Hooker process, in which benzene is chlorinated to chlorobenzene by the reaction of benzene with HCl and oxygen over copper chloride on an inert support.

Chlorides of rare earths and alkali metals often serve as promoters for CuCl_2 in oxychlorination. Workers at the M. W. Kellogg Company (60) have described a homogeneous version of the oxychlorination process, using an aqueous solution of copper salts. This has the advantage of easy heat removal by water evaporation.

d) Hydrogen cyanide

The formation of hydrogen cyanide from ammonia, methane, and oxygen over rhodium or iridium-promoted platinum was disclosed by Andrussov some time ago ($\text{CH}_4 + \text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$) and was commercialized using promoted platinum gauze, similar to the process used to make nitric acid from ammonia. An improvement of the Andrussov process was commercialized in the 1950s by Degussa. In this process, small diameter refractory tubes are coated with the catalyst and the reaction proceeds on the reactor walls. In this case no oxygen is required and the process produces hydrogen according to $\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2\text{O}$.

X OLEFIN DISPROPORTIONATION CATALYSIS

A new catalytic reaction was disclosed by Banks and Bailey in 1964.^(61;62) Called "olefin disproportionation," it converted linear olefins into homologs of shorter and longer chains in a highly specific and efficient manner. The total moles of product olefins heavier than the feed equaled the total moles of lighter olefins. Propylene for example could be converted to ethylene and butenes ($2\text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{C}_4\text{H}_8$). While the original discovery involved the use of molybdenum or tungsten hexacarbonyl catalysts supported on alumina, many other catalysts--both heterogeneous and homogeneous--have since been reported for this reaction.⁽⁶³⁾ Table 4 shows some of the heterogeneous support and promoter combinations used. Typical homogeneous catalysts described in the literature are those obtained by interaction of tungsten hexachloride, ethanol, and ethylaluminumdichloride, or by reaction of nitrosyl complexes of halides.

The first commercial application of the new process chemistry occurred in 1966. Shawinigan Chemicals Company in Canada installed a Phillips Petroleum Company "Triolefin" process unit to convert propylene into polymerization-grade ethylene and high purity butenes. Other installations have been installed since then.

XI INDUSTRIAL HOMOGENEOUS CATALYSIS

Applications of homogeneous catalysis have greatly increased in recent years. Where sulfuric acid catalysed alkylation and the cobalt carbonyl catalysed Oxo reaction ($\text{CH}_3\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{C}_3\text{H}_7\text{CHO}$) were almost alone in this field 25 years ago, there are now over 20 industrial processes. Most employ soluble metal compounds as catalysts. Monomers and polymers are the major products. G. W. Parshall has recently published a review of homogeneous catalytic processes,⁽⁶⁴⁾ and Table 5 summarizes some major applications.

Table 4⁽⁶³⁾Olefin Disporportionation Catalyst Supports
and Promoters

	Supports			Promoters		
OXIDES	Al	Si	Fe	Mo	W	Re
	Ni	Zr	Sn	Nb	Rh	Sn
	W	Th	SiAl	Te	La	Ta
	AlTi	AlTh	MgSi	Os	Ir	
	MgTi					
PHOSPHATES	Al	Ti	Ca			
	Zr	Mg				
HEXACARBONYLS				Mo	W	Re
SULFIDES				Mo	W	

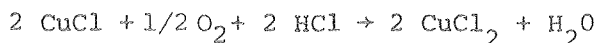
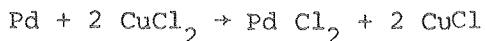
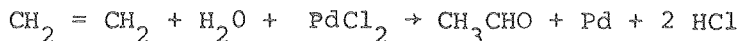
Table 5⁽⁶⁴⁾Major Applications of Homogeneous Catalysis
in the U.S. Chemical Industry

	Approximate 1975 capacity or pro- duction (thousands of metric tons)
Carbonylations	
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2 \longrightarrow \text{C}_3\text{H}_7\text{CHO}$ (includes other oxo products)	650 p
$\text{RCH}=\text{CH}_2 + \text{CO} + 2\text{H}_2 \longrightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{OH}$	170 c
$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$	190 c
Monoolefin Reactions	
$\text{CH}_2=\text{CH}_2 + \text{O}_2 \longrightarrow \text{CH}_3\text{CHO}$	410 p
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{ROOH} \longrightarrow \text{CH}_3\text{CH} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH}_2 + \text{ROH}$	250 c
$\text{CH}_2=\text{CH}_2 \longrightarrow \text{Polyethylene}$ (excludes oxide supported catalysts)	150 c
$\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}=\text{CH}_2 + \text{diene} \longrightarrow \text{EPDM rubber}$	85 p
Diene Reactions	
$3\text{CH}_2=\text{CHCH}=\text{CH}_2 \longrightarrow \text{cyclododecatriene}$	10 p
$\text{C}_4\text{H}_6 + \text{CH}_2=\text{CH}_2 \longrightarrow 1,4\text{-hexadiene}$	2 p
$\text{C}_4\text{H}_6 + 2\text{HCN} \longrightarrow \text{NC}(\text{CH}_2)_4\text{CN}$	70 c
$\text{C}_4\text{H}_6 \longrightarrow \text{cis-1,4-polybutadiene}$	290 p
Oxidations	
$\text{c-C}_6\text{H}_{12} \xrightarrow{\text{O}_2} \text{c-C}_6\text{H}_{11}\text{OH} + \text{c-C}_6\text{H}_{10}=\text{O} \xrightarrow[\text{HNO}_3]{\text{O}_2 \text{ or}} \text{adipic acid}$	610 p
$\text{c-C}_{12}\text{H}_{24} \xrightarrow{\text{O}_2} \text{c-C}_{12}\text{H}_{23}\text{OH} + \text{c-C}_{12}\text{H}_{22}=\text{O} \xrightarrow[\text{HNO}_3]{\text{HNO}_3} \text{dodecanedioic acid}$	10 c
$\text{CH}_3 \text{---} \langle \text{benzene ring} \rangle \text{---} \text{CH}_3 \xrightarrow{\text{O}_2} \text{terephthalic acid and esters}$	2 100 p
$\text{n-C}_4\text{H}_{10} \xrightarrow{\text{O}_2} \text{CH}_3\text{COOH}$	470 p
$\text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COOH}$	335 p
Other Reactions	
$\text{CH}_2=\text{CHCHClCH}_2\text{Cl} \rightleftharpoons \text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	270 p
$\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl} + 2\text{NaCN} \longrightarrow \text{NCCH}_2\text{CH}=\text{CHCH}_2\text{CN}$	125 c
$\text{ROOC} \text{---} \langle \text{benzene ring} \rangle \text{---} \text{COOR} + \text{HOCH}_2\text{CH}_2\text{OH} \longrightarrow \text{polyester}$	1 900 p

Olefin polymerization is probably the largest scale application of organometallic catalysed processes. Many of the catalysts used in the process technology initiated by Ziegler and Natta⁽⁷²⁾ are not soluble and therefore are discussed separately. However, a significant amount of linear polyethylene is produced with soluble titanium catalysts. Ethylene-propylene-diene elastomers and stereoregular polybutadiene are produced with analogous catalyst mixtures based on other transition metal compounds.

In 1938-1946 Roelen in Germany developed the Oxo process, still one of the largest applications of homogeneous catalysis. It involves hydroformylation, the reaction of an olefin with carbon monoxide and hydrogen to produce aldehydes (e.g., butyraldehyde from propylene or propionaldehyde from ethylene) and fatty alcohols from higher olefines. Cobalt carbonyls were the usual catalysts.⁽⁶⁵⁾ They were generated in-situ from cobalt salts and synthesis gas ($\text{CO} + \text{H}_2$) in the presence of a base. They are used at 200-300 atm. pressure and 100-150 °C. A major improvement in catalyst technology was made when Union Carbide commercialized in 1976 the production of butyraldehyde from xylene employing homogeneous rhodium catalysts containing a phosphine ligand. The new catalysts operate at much lower pressure, e.g., 10-25 atm. and at low temperature (~ 100 °C).

In 1960, a major advance in metallorganic catalysis occurred when Wacker Chemie, a subsidiary of Höchst, introduced a simple high-yield process for producing acetaldehyde from ethylene.⁽⁶⁶⁾ This process practiced in the United States by companies such as Celanese and Texas Eastman has largely displaced syntheses based on ethanol or acetylene. The oxidation of ethylene is carried out either as a two-stage process using air, or as a one-stage process using oxygen. The oxidizing catalyst is an aqueous solution of cupric chloride and palladium chloride and proceeds in three steps:



Ethylene is oxidized by water and palladium chloride. The resulting palladium metal is reconverted to palladium chloride by cupric chloride. The cuprous chloride is reoxidized by air or oxygen. Farbenfabriken Bayer has introduced a heterogeneous version of this catalyst. The same type of homogeneous catalysis is also used to produce vinyl acetate from ethylene and acetic acid.

Acetic acid is produced by oxidation of acetaldehyde with soluble metal catalysts. The largest type of process, though, is based on the carbonylation of methanol.⁽⁶⁷⁾ Badische Anilin and Sodafabrik (BASF) pioneered a process that has been used in the U.S. by Borden Chemical Company since 1968. It uses a cobalt carbonyl catalyst promoted by iodine. More recently, Monsanto commercialized in 1977 a process employing rhodium complexes and methyl iodide as cocatalysts.⁽⁶⁸⁾ The Monsanto process uses milder process conditions and exhibits very high selectivity to acetic acid, but must, to be economical, recover almost all of the rhodium.

According to Parshall, one of the largest applications of homogeneous catalysis is the production of terephthalate esters. P-xylene is oxidized by air using soluble cobalt and manganese salts as catalysts. Amoco Chemicals Company is a major user of this process.

An interesting new process was discovered and commercialized in 1969 by Oxirane Corporation.⁽⁶⁹⁾ Propylene is oxidized to propylene oxide by t-butyl hydroperoxide, catalysed by soluble molybdenum compounds such as molybdenum carbonyl. The t-butylhydroperoxide is obtained by air oxidation of isobutane. T-butyl alcohol is a co-product with propylene oxide. This process is finding application

in various parts of the world and is replacing older methods of propylene oxide manufacture.

Also, in 1969 the M.W. Kellogg Company announced a different type of homogeneously catalysed process, a new version of the old Deacon process to convert HCl to chlorine. The "Kelchlor" process⁽⁷⁰⁾ has been commercialized on a large scale by E.I. duPont de Nemours & Company. It uses oxides of nitrogen as the catalyst in combination with a powerful dehydrating agent, H_2SO_4 . The latter permits the reaction to proceed beyond equilibrium constraints, since it effectively removes water of reaction from the reaction product. The process is of particular use in conjunction with chlorination reactions, since it permits the by-product HCl to be reconverted to chlorine.

A very large-scale application of dissolved catalysts is the production of dichloroethane from ethylene and chlorine, employing $FeCl_3$, $CuCl_2$, or $SbCl_3$. The dichloroethane is then thermally dehydrochlorinated to vinyl chloride.

XII CATALYTIC POLYMERIZATION

Polymerization catalysis is an important and relatively old field. Before and during the second World War, efforts were largely concentrated on dimerizing and trimerizing ethylene and propylene to high-octane gasoline.⁽⁷¹⁾ Work was also done to obtain higher molecular weight products in the lubricating oil boiling range. With the need for synthetic rubber spiraling during World War II, technology was developed for butadiene polymers and butadiene-styrene as well as isobutylene-isoprene copolymers. Numerous improvements have been made in the polymerization of these and other monomers, such as vinyl chloride, which cannot be enumerated here.

After World War II the polymer industry began to develop rapidly, and polyethylene--and to a somewhat lesser extent polypropylene--became articles of large-scale commerce. The high-pressure polyethylene

process commercialized by Imperial Chemical Industries in England, BASF in Germany, and others involved a thermal free radical process at pressures of 1000 atm. and more, and it dominated the field until major discoveries were made by Karl Ziegler in Germany and G. Natta in Italy. These men later shared a Nobel Prize in 1964 for their contributions.

Ziegler disclosed in 1955 a catalyst system⁽⁷²⁾ that would polymerize ethylene to polyethylene at low pressures, e.g., 10 atm. (The "low-pressure" polyethylene is more linear, has a higher melting point, and is more rigid than "high-pressure" polyethylene.) Catalysts spanning the homogeneous-heterogeneous interface were used (see also the section on Homogeneous Catalysis). One such catalyst is prepared from aluminum alkyl, e.g., Al Et_3 and titanium tetrachloride, using an excess of the alkyl.⁽⁷³⁾ The preparation is carried out in a dry hydrocarbon solvent, usually hexane. The precipitate plus the aluminum alkyl still in solution is "the catalyst." The reaction is carried out at 50-75 °C and about 10 atm. pressure, and the polymer forms as a white powder suspended in the solvent. Many catalyst modifications have been developed by various manufacturers. In the Amoco Chemical Company process,⁽⁷⁴⁾ which operates at 240-300 °C and 35-100 atm. pressure, the catalyst is molybdic acid on alumina, plus reducing agents such as aluminum alkyl, lithium borohydride, or metallic sodium as co-catalysts. The Phillips Petroleum Company catalyst⁽⁷⁵⁾ comprises chromium trioxide on silica or alumina in cyclohexane as the solvent. Promoters are used, as shown in Table 6.⁽⁷⁶⁾

G. Natta in 1969 described the polymerization of propylene and higher α -olefins to highly ordered, crystalline polymers. "Isotactic" polypropylene has the carbon atoms in each succeeding propylene unit ordered in the same identical way. C. L. Thomas⁽⁷³⁾ refers to a statement by Natta that the term "isotactic" was suggested by Mrs. Natta because the structure reminded her of the ordered lines and columns of marching soldiers.

Table 6⁽⁷²⁾

Some Oxide Promoters for Supported Chromia Catalysts

SUPPORT →	SiO ₂	Al ₂ O ₃	ZrO ₂	ThO ₂
PROMOTER ↓	CuO			
	ZnO	ZnO		
	SrO	SrO		
	WO ₃			
	Mn ₂ O ₃	Mn ₂ O ₃		
	Co ₂ O ₃			
	Fe ₂ O ₃			
		MgO		
		BaO	BaO	
		B ₂ O ₃		

Natta requires a crystalline or microcrystalline catalyst for the production of stereospecific products. Crystalline α -titanium trichloride plus aluminum alkyl constitutes such a catalyst system. Operating conditions of this type of catalyst for propylene polymerization are similar to Ziegler's, except for slightly higher temperatures.

The Ziegler and Natta discoveries have resulted in applications of great technological importance, and over one-half of all olefin polymers produced is based on this technology.

Urethane foams constitute an important item of plastics manufacture. They are obtained from isocyanates and alcohols, particularly diols in the presence of some water. The reaction is catalytic and most of the product is manufactured using a catalyst first introduced in 1959 by Houdry Process Corporation, called "Dabco" (triethylene diamine).⁽⁷⁷⁾ This is often promoted by organic stannous compounds. The commercial use of this catalyst combination appears to have been the first introduction of an organic compound as a catalyst. DABCO has such high activity that it permits a one-step process.

XIII CATALYSIS FOR MOTOR VEHICLE EMISSION CONTROL⁽⁷⁸⁾

It is a rare event when a whole new field of catalytic applications opens up. This happened when the State of California enacted laws on air quality and motor-vehicle emissions standards in 1959 and 1960. These laws were to go into effect when at least two devices had been developed that could meet these standards. While these laws stimulated a considerable amount of research, one should not omit mention of the fact that Eugene J. Houdry, the pioneer of so much industrial catalysis (see sections on Catalytic Cracking and Dehydrogenation), foresaw the need for emission control--at least in confined spaces--as early as 1949, and developed catalytic mufflers for indoor vehicles, marketed by Oxy-Catalyst, Inc. One of these early catalysts consisted of monolith-porcelain rods covered

with alumina upon which platinum was deposited. This anticipated later developments.

Following the California law enactment, three groups of catalyst and muffler manufacturers were certified by the California Motor Vehicle Control Board in 1964 and 1965. These were W. R. Grace—Norris Thermador, Universal Oil Products—Arvin, and American Cyanamid—Walker. However, engine modifications by the car manufacturers enabled them to meet specifications without the use of catalysts.

The U.S. Federal Clean Air Act of 1970 set requirements that could not be met by existing technology, and this spurred an intensive research effort. Although enforcement of the law was later delayed by one year, from 1975 to 1976, and the law was modified by setting interim standards, catalytic mufflers have been installed on all new cars in the U.S. since 1976. The only exception has been Honda cars which used an improved mechanical system.

Among the numerous organizations doing research and development in this area during this period was a combination of companies doing joint research in the "Interindustry Emission Control Program." The group consisted of Ford Motor Company, Mobil Oil Corporation, Volkswagen, Toyota, Fiat, and others.

The initial objective of emission control research was to reduce carbon monoxide and hydrocarbon emissions to specified levels, 90 percent or more below those previously emitted. The reduction of nitrogen oxide emissions was undertaken somewhat later. A totally new problem for catalytic reactor design was immediately recognized. While most industrial catalytic operations involve continuous and steady-state conditions, automobile operations are intermittent and transient, with wide fluctuations of flow rate and temperature that depend on driving conditions and cold or warm engine starts.

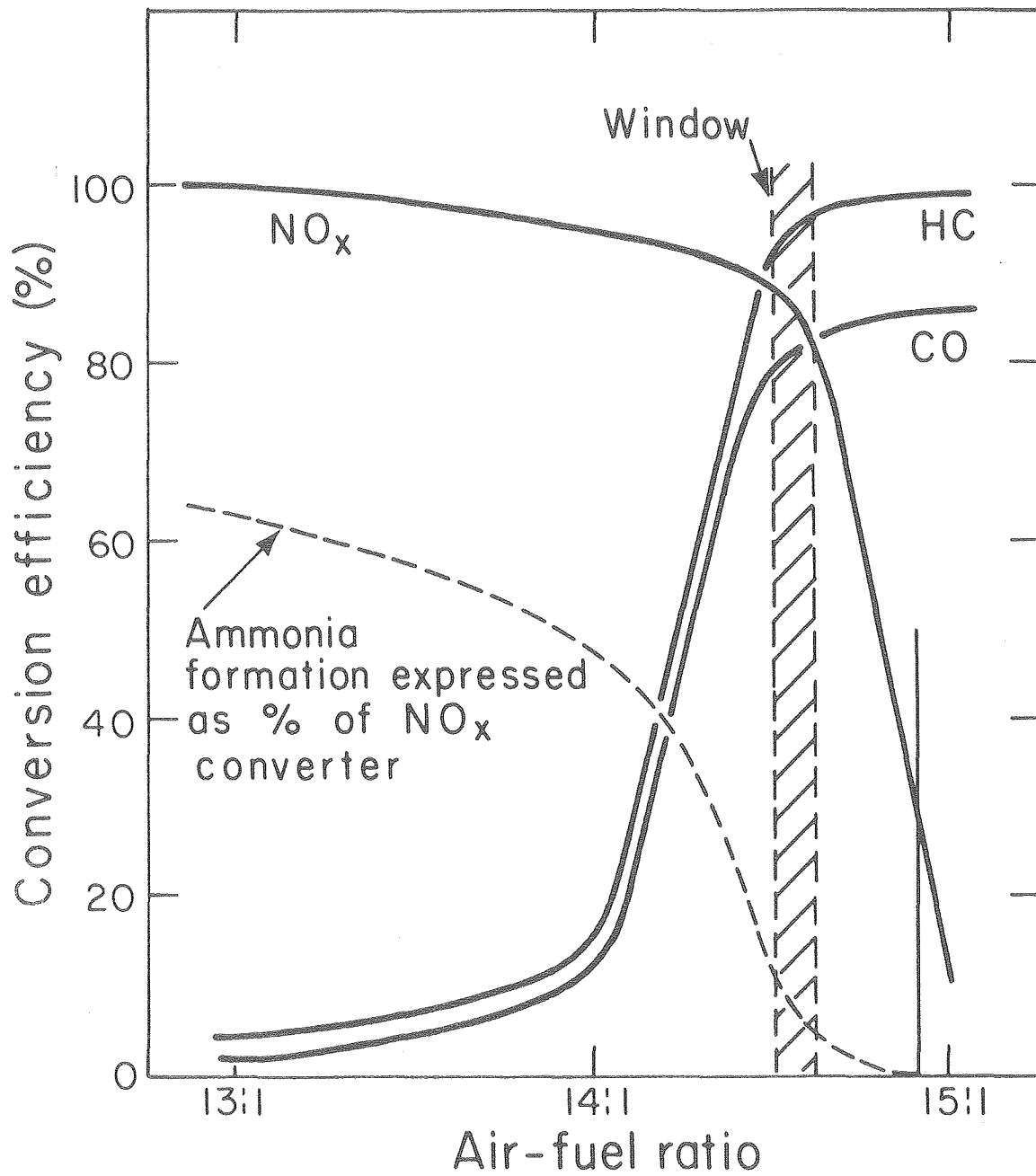
As shown in J. Wei's review of the field,⁽⁷⁸⁾ exhaust gas-flow rates can vary from 20 to more than 200 SCF/min, and

exhaust temperatures from 600 to 1800 °F (351-980 °C) plus. Many materials such as base-metal oxides and alloys oxidize CO and hydrocarbons to CO₂ at quite high conversions. Requirements are, however, that more than 90 percent of CO and hydrocarbons be removed at space velocities of up to 200,000 V/V/hr within a temperature range of about 500-2000 °F. (260-1100 °C) In addition, the oxidizing atmosphere contains 15 percent water and not much more than a stoichiometric amount of oxygen. The catalyst, further, must last for at least 25,000 vehicle miles.

Only precious metal catalysts have thus far been used commercially to meet the many difficult specifications. In most cases, the metal is dispersed as small crystallites on thermally stable, chemically inactive supports such as α-alumina. Three major support shapes comprise spheroids, wire mesh, and monolithic honeycombs. A "washcoat" of high-surface-area alumina is usually placed on the ceramic surface and acts as substrate for the precious metal

A major requirement for the use of platinum-type emission catalysts has been the elimination of potential poisons from the gasoline, most prominently the lead compounds. All cars having catalytic mufflers must use lead-free gasoline. This has resulted in the inability to boost octane number by addition of tetraethyl lead to gasoline, and in the need to produce relatively high-octane (91-93 Research) gasoline by catalytic reforming or cracking; it has increased the amount of crude oil processed, since yield of gasoline decreases with increasing octane requirement.

The amount of precious metal used in emission control devices is about 0.05 troy oz/car. Reactor design is complex, since high pressure drop must be avoided at very high space velocities. Manufacturers of commercial emission control catalysts in the U.S. include Engelhard, W. R. Grace & Company, Universal Oil Products Company, The Catalyst Company, and the Houdry Process Division of Air Products & Chemicals, Inc.



XBL 796-1707

Fig. 15. "Three-way" Redox Catalyst Conversion Characteristics.

Figure taken from reference 78.

In addition to CO and hydrocarbon emission standards, specifications for NO_x emissions have been set for 1977 and later cars in the United States. Three-way precious metal "Redox" catalysts can take advantage of a "window" at an air/fuel ratio of exactly 14.7:1, at which NO_x conversion is still high and CO and hydrocarbon conversion is very substantial (all conversions > 80%)(Fig.15.) However, the window is so narrow that maintenance of this air/fuel ratio is difficult. Proposals for a separate NO_x catalyst bed have thus far not been commercialised. For the total catalytic system, two converters or a converter containing a dual-bed catalyst will probably be necessary. The first bed will catalyse the reduction of nitrogen oxides to nitrogen, while the second oxidizes hydrocarbons and CO to CO₂ and water. Three-way converters will be required to meet the 1981 standards.

Development of catalysts for automotive emission control has been and is a great challenge because of the extreme mechanical and operating condition variations encountered. The use of catalysts in cars in 1978 is shown in Table 7.⁽¹⁷⁾

XIV FUEL CELL CATALYSIS

Catalysts are used at both the anode and cathode of a fuel cell. Hydrogen has been the most common fuel. It is oxidized at the anode and the oxidant is reduced at the cathode. While much research has been undertaken on fuel-cell catalysis, industrial applications are thus far very limited. Fuel cells were used in the Gemini and Apollo space crafts using noble metal on carbon catalysts. A large electric utility demonstration is planned by Consolidated Edison in New York for 1979. This unit will generate about 5 megawatts.⁽⁷⁹⁾

XV THE PROFESSION OF CATALYTIC CHEMISTS AND ENGINEERS

While catalysis as it has been discussed is an old art and quite old a science, until the last quarter of this century it has functioned essentially as a part of various branches of

Table 7⁽¹⁷⁾Use of Catalysts in Cars
in 1978

Material	Estimated use*	Estimated value* (million dollars)
Alumina pellets	37.6 million lbs.	\$71.0
Cordierite monolith	8.9 million lbs.	34.0
Alumina wash coat	1.6 million lbs.	1.4
Platinum	395,000 troy oz.	93.6
Palladium	130,000 troy oz.	9.2
Total		\$209.2

*For installation on cars manufactured in the U.S. last year.
Actual use would be at least 10% higher because of
converters for Canadian cars and spares.

of chemistry (physical, organic, inorganic), physics, and engineering (reactor engineering, modeling).

A first international meeting, primarily devoted to catalytic research, was held by the Faraday Society in 1949. The annual Gordon Research Conferences on Catalysis started in 1943 as the Gibson Island Conferences, and moved to Colby Junior College in New Hampshire in 1946 as part of the Gordon Research Conference. A whole generation of catalytic scientists has attended these prestigious and pleasant meetings restricted to about 100 persons.

In 1949, a group of seven scientists gathered in Philadelphia to discuss the possibility of holding regular local meetings in the field of catalysis. They were A. Farkas, F. G. Ciapetta, R. Hansford, H. Heinemann, R. Kennedy, K. A. Krieger, and A. G. Oblad. These men started the Catalysis Club of Philadelphia, which from that time on held monthly meetings. All of the founders served as chairmen of the Club in its early years. First-year meetings were held at the University of Pennsylvania, and attendance at the meetings rapidly increased from about 15 to 80-100 persons. Men prominent in the field like D. A. Dowden, P. H. Emmett, and Otto Beek, were among the first speakers. Beginning in 1951 an annual all-day symposium was held--a custom that still prevails. The first symposia were on Saturdays at Swarthmore College, then at the DuPont Country Club in Wilmington, and later in Princeton, New Jersey and in Chester, Pennsylvania. Membership of the Philadelphia Club rapidly increased to above 200 and has remained at that level. A Chicago Catalysis Club was founded a few years later, followed by the New York Club--whose founders were charter members of the Philadelphia Club. Within the next 20 years, catalysis clubs were formed in California, New England (Boston), Pittsburgh, Houston (Southwest Catalysis Club), Michigan, and also in Canada. In 1979, the Tri-State Catalysis Society joined the group.

In 1954, Rudolf Brill and Heinz Heinemann suggested to the Philadelphia Club that an International Congress on Catalysis should be held, and the Club under its chairman, G. A. Mills enthusiastically sponsored the First International Congress of Catalysis in Philadelphia in 1956. P. H. Emmett, Eric Rideal, and Eugene Houdry were honorary chairmen, and Heinz Heinemann was executive secretary of the event with responsibility for the overall organization. Numerous committee chairmen worked hard to make the Congress a success and they, as well as the sponsors who contributed \$43,000 to the Congress, are listed in Volume 9 of *ADVANCES IN CATALYSIS* that contains the proceedings of the meeting. The Congress was attended by over 600 persons, many of whom came from abroad with the support of part of the funds raised for the event. During preparations for the meeting, the "International Congress on Catalysis" was incorporated in the U.S., and at the meeting it was decided to hold such Congresses once every four years in a country offering an invitation. Heinz Heinemann was elected president of the organization for the period 1956-1960 and through the second Congress held in Paris in 1960. He was succeeded as president by A. Farkas (1960-1964), F. G. Ciapetta (1964-1968), and V. Haensel (1968-1972). The Third Congress was held in Amsterdam in 1964, the fourth in Moscow in 1968, the fifth in Palm Beach, Florida in 1972, the sixth in London in 1976, and the seventh is scheduled for 1980 in Tokyo. All Congresses after the first five were attended by at least 1000 participants, and proceedings have been published for all of them. The Second Congress was cosponsored by IUPAC, and subsequent ones were joint enterprises. After the success of the Second Congress, a truly international organization was established with a board comprising two representatives from each member country. Local organizing committees did most of the work.

By 1965, the individual catalysis clubs in the United States felt the need for closer affiliation, and the Catalysis Society of North America was established, which comprised the membership of

all catalysis clubs that were renamed "Catalysis Society of California," etc. The organization of the Catalysis Society and of its first national meeting in Atlantic City in 1969 were financed with funds remaining from the First International Congress on Catalysis. National meetings of the Society have been held every two years in odd-numbered years in Atlantic City, New Jersey, Houston, San Francisco, Toronto, Pittsburgh, and Chicago. All have been attended by hundreds of participants and parallel scientific sessions have been required. The Society is administered by a Board of Directors elected by the member societies and the membership at-large. The Board in turn elects a president, or vice-president, secretary, and treasurer.

In 1967, the Catalysis Society of North America proposed the establishment of two prestigious awards to be given once every two years. A committee comprised of A. H. Weiss and Heinz Heinemann obtained sponsorship for the "Paul H. Emmett Award" in fundamental catalysis and the "Eugene J. Houdry Award" in applied catalysis--the former to carry a \$2000 prize and the latter a \$2500 prize. The Emmet Award has been sponsored since its inception by the Davison Division of W. R. Grace & Company; the Houdry Award was originally sponsored by the Houdry Process Corporation, Sun Oil Company, Oxycat Corporation, and the Houdry family. More recently, Air Products and Chemicals Corporation has taken over a good part of the sponsorship. Award winners for the first ten years were:

<u>Emmett Award</u>	<u>Houdry Award</u>
R. Kokes	H. Bloch
J. H. Sinfelt	C. Plank
J. Lunsford	H. Heinemann
G. A. Somorjai	V. Haensel
G. Ertl	A. Farkas

Catalysis Clubs have also prospered in other countries. There are now such groups in Hungary, Japan, and Holland.

The Gordon Conferences found a European equivalent in the Roremont Conferences held in Holland for the past ten years.

ACKNOWLEDGEMENT

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» Houdry Process for Catalytic Cracking

Houdry Process for Catalytic Cracking

National Historic Chemical Landmark

Dedicated April 13, 1996, at the Sun Company (now Sunoco Logistics Partners L.P.) in Marcus Hook, Pennsylvania.

[Commemorative Booklet \(PDF\)](#)

The first full-scale commercial catalytic cracker for the selective conversion of crude petroleum to gasoline went on stream at the Marcus Hook Refinery of Sun Company (now Sunoco, Inc.) in 1937. Pioneered by Eugene Jules Houdry (1892-1962), the catalytic cracking of petroleum revolutionized the industry. The Houdry process conserved natural oil by doubling the amount of gasoline produced by other processes. It also greatly improved the gasoline octane rating, making possible today's efficient, high-compression automobile engines. During World War II, the high-octane fuel shipped from Houdry plants played a critical role in the Allied victory.

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Houdry's Challenge: Transforming Crude Oil into Gasoline

Commercial production of petroleum began in Titusville, Pennsylvania, in 1859. The internal combustion engine was developed soon after, and the first gasoline-fueled "horseless carriages" appeared on American streets in 1895. But since only wealthy people could afford them, there were probably no more than 8,000 automobiles in the United States by the turn of the century.

Crude petroleum is a complex mixture of hydrocarbon molecules — compounds containing carbon — and hydrogen atoms. Initially, crude petroleum was separated by distillation into fractions distinguished by differences in their boiling points. Some higher-boiling fractions were used for lighting and some for lubrication, but for many years, little use was found for the gasoline component.

As the number of automobiles, trucks and tractors increased, the demand for gasoline increased, and by 1910 when there were 500,000 automobiles, a gasoline shortage had developed. It occurred to a few perceptive inventors that it might be possible to produce additional gasoline from the unused, higher-boiling petroleum fractions. In 1913, Dr. William Burton of Standard Oil of Indiana introduced a thermal-cracking procedure that used high temperature and pressure to break down the larger, higher-boiling molecules into the smaller, lower-boiling molecules found in gasoline.

It was recognized that more efficient engine performance could be achieved from a fuel that had a higher "octane rating," the measure of a fuel's efficiency in a standard engine. The first significant increase in octane

rating was obtained in 1923, when Standard Oil of Indiana, using a discovery of Thomas Midgley, Jr., of General Motors, added tetraethyl lead to gasoline.

In the early 1920s, the French engineer Eugene Jules Houdry began his search for a catalyst to produce gasoline from lignite. A catalyst is a substance that can increase the rate at which a chemical reaction occurs, without itself being changed. Because it has the potential to produce very selective results, such as the cracking of high-boiling petroleum fractions to gasoline, a catalyst can give a particular process a competitive advantage. In the 1920s, the science of catalysis was still in its infancy, and the business applications were limited to the hydrogenation of vegetable oils to make butter substitutes, the conversion of atmospheric nitrogen to make ammonia for fertilizers and explosives, and the conversion of carbon monoxide to make methanol or hydrocarbons. The Gulf Oil Corporation had tried to replace the energy-intensive thermal cracking of the higher-boiling petroleum fractions with an aluminum chloride catalyst, but the results were not economically successful because the cost was too high.

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Development of the Houdry Process

As an avid participant in the sport of automobile racing, Eugene Houdry was acutely aware of the importance of high-performance fuels for successful machine performance. As a Frenchman, Houdry was also aware of the growing need for gasoline in a country that was deficient in its own petroleum resources.

In 1922, Houdry learned about an exceptional gasoline derived from lignite that was being produced in a catalytic procedure by E. A. Prudhomme, a pharmacist in Nice, France. Houdry visited Prudhomme and persuaded him to move to Beauchamp, near Paris, where Houdry and some of his business associates financed and set up a laboratory. For the next few years, Houdry worked closely with Prudhomme and others to develop a workable lignite-to-gasoline process.

Supported by the French government, Houdry's syndicate built a demonstration plant that processed 60 tons of lignite per day to produce oil and gasoline. The plant started operations in June 1929, but the results were disappointing and the process was not economically competitive. The government subsidy was withdrawn, and the plant was shut down in that same year.

During the lignite-to-gasoline process, the solid lignite was initially broken down by heat to produce viscous hydrocarbon oil and tars, then the oil was further converted by an added catalyst to produce lower-boiling hydrocarbons similar to the gasoline fraction derived from petroleum. Although much emphasis had been placed by others on nickel-containing catalysts, Houdry discovered that a clay mineral named Fuller's Earth, a naturally occurring aluminosilicate, could convert the oil derived from lignite to a gasoline-like product. Working with this knowledge, Houdry focused his attention on the application of catalysis to petroleum processing.

In 1930, H. F. Sheets of the Vacuum Oil Company learned of Houdry's promising results using a catalyst to convert vaporized petroleum to gasoline, and invited him to come to the United States. After a successful trial run, Houdry moved his laboratory and associates from France to Paulsboro, New Jersey.

The Houdry Process Corporation was founded in 1931, a joint venture of Houdry with his associates at the Vacuum Oil Company. That same year, Vacuum Oil merged with Standard Oil of New York to form the Socony-Vacuum Oil Company (later Mobil Oil Corporation). In 1933, a 200-barrel-per-day Houdry unit was put in operation. But the Great Depression had weakened the oil business. Unable to finance Houdry's work any further, Socony-Vacuum gave him permission to seek support from other petroleum companies.

In late 1933, Houdry met with Sun Oil Company (later Sun Company) president J. Howard Pew and vice president for refining Arthur Pew, Jr. Shortly thereafter, Houdry, Socony-Vacuum and Sun signed a joint

development agreement. In the next few years, the Houdry process underwent further changes, including an innovative method for regenerating the catalyst after a short, ten-minute usage time.

These results inspired Socony-Vacuum and Sun to proceed to commercialization. In April 1936, Socony-Vacuum converted an older thermal-cracking unit in Paulsboro into a semi-works unit using the Houdry process. In March 1937, Sun's new, fully commercial unit went into operation. Processing 15,000 barrels of petroleum per day, this unit featured such innovations as a molten-salt heat control technique and motor-operated valves controlled by timers. Almost 50 percent of the product was high-octane gasoline, compared with 25 percent from the more conventional thermal processes.

When Arthur Pew, Jr., presented the details of the successful commercial process at a 1938 meeting of the American Petroleum Institute, the industry was astounded. An article in *Fortune* magazine, entitled "Monsieur Houdry's Invention," said Pew "had dropped a bombshell." In 1940, the first large-scale plant for producing a synthetic silica-alumina catalyst began operations in Paulsboro.

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A NATIONAL HISTORIC
CHEMICAL LANDMARK

THE HOUDRY PROCESS

FOR THE CATALYTIC CONVERSION OF CRUDE
PETROLEUM TO HIGH-OCTANE GASOLINE

SUN COMPANY
MARCUS HOOK, PENNSYLVANIA

APRIL 13, 1996



AMERICAN CHEMICAL SOCIETY

Division of the History of Chemistry and
The Office of Public Outreach

"The Houdry Process" commemorative booklet produced by the National Historic Chemical Landmarks program of the American Chemical Society in 1996 (PDF).

Impact of the Houdry Process

The invention and development of gasoline-fueled motor vehicles has had a profound influence on human history providing transport for industrial products and employment for millions and determining where and how we live, work and play. In the United States today, more than half of the 300 million gallons of gasoline used each day to fuel more than 150 million passenger cars is produced by catalytic-cracking technology. High-

octane gasoline paved the way to high compression-ratio engines, higher engine performance and greater fuel economy.

The most dramatic benefit of the earliest Houdry units was in the production of 100-octane aviation gasoline, just before the outbreak of World War II. The Houdry plants provided a better gasoline for blending with scarce high-octane components, as well as by-products that could be converted by other processes to make more high-octane fractions. The increased performance meant that Allied planes were better than Axis planes by a factor of 15 percent to 30 percent in engine power for take-off and climbing; 25 percent in payload; 10 percent in maximum speed; and 12 percent in operational altitude. In the first six months of 1940, at the time of the Battle of Britain, 1.1 million barrels per month of 100-octane aviation gasoline was shipped to the Allies. Houdry plants produced 90 percent of this catalytically-cracked gasoline during the first two years of the war.

The original Houdry process embodied several innovative chemical and engineering concepts that have had far-reaching consequences. For example, the improvement of the octane rating with catalytic processes showed that the chemical composition of fuels was limiting engine performance. Further, aluminosilicate catalysts were shown to be efficient in improving the octane rating because they generated more highly branched isoparaffins and aromatic hydrocarbons, which are responsible for high octane ratings. From an economic standpoint, the catalysts could be regenerated after a short usage time, thus returning the catalyst to full activity without having to add additional material.

The original fixed-bed Houdry Process units have been outmoded by engineering advances that transformed the fixed-bed to more economical [fluidized-bed systems](#) and introduced the use of crystalline aluminosilicate catalysts to provide higher yields of gasoline. Yet it is remarkable that, seventy years after Houdry's discovery of the catalytic properties of activated clay to convert petroleum fractions to gasoline, the same fundamental principles that made the process a success are still the primary basis for manufacturing gasoline worldwide.

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Biography of Eugene Jules Houdry

Born near Paris, France, on April 18, 1892, Eugene Jules Houdry was the son of a wealthy steel manufacturer. He studied mechanical engineering at the Ecole des Arts et Métiers in Chalons-sur-Marne, a Paris suburb. He graduated in 1911, earning the French government's gold medal for the highest scholastic achievement in his class. He was captain of his school's soccer team, which won the championship of France that same year.

Houdry joined his father's business, but left for military training right before the outbreak of World War I. He served in the French army as a lieutenant in the tank corps and in 1917 was seriously wounded in the battle of Juvincourt, winning the Croix de Guerre for his actions and later becoming a Chevalier of the Legion of Honor.

After the war, Houdry rejoined his father at Houdry et Fils, but by 1922 was making his way in the field of catalytic processes for the conversion of coal and lignite to gasoline. His interest in high-octane gasoline was fueled by his avid interest in automobile engines and in road racing, where he competed in a Bugatti racing car.

In addition to the process for high-octane gasoline, Houdry also invented a catalytic process for the production of butadiene from the butane gas derived from crude oil production. Butadiene became an important resource during World War II. It was one of the two components used in the synthetic rubber program initiated after natural rubber supplies were eliminated by the war in the Pacific.

Houdry was outspoken in his opposition to wartime collaboration with the Germans by the French Vichy government of Marshall Henri Pétain. On May 3, 1941, the Vichy government declared that Houdry had lost his French citizenship. He then became president of the U.S. chapter of "France Forever" — an organization dedicated to the support of General Charles de Gaulle, the nominal head of the French government in exile — and in January 1942, he became a United States citizen. His two sons, Jacques and Pierre, served in the

United States Army during World War II, and Houdry directed his efforts toward industrial processes crucial to the war effort.

After World War II, Houdry formed the Oxy-Catalyst Company and turned his attention to reducing the health risks associated with the increasing amounts of automobile and industrial air pollution. His generic catalytic converter, which greatly reduced the amount of carbon monoxide and unburned hydrocarbons in automobile exhausts, was granted U.S. Patent 2,742,437 in 1956. Today, catalytic converters made by various companies are standard devices on all American cars.

Houdry's colorful life was full of great ambitions. His unusually productive career was characterized by unique foresight, bold imagination, creative leadership, persistence and, above all, action. Houdry's contributions to catalytic technology were recognized by numerous awards, including the Potts Medal of the Franklin Institute in 1948, the Perkin Medal of the Society of Chemical Industry (American Section) in 1948, the E. V. Murphree Award in Industrial and Engineering Chemistry of the American Chemical Society in 1962, and posthumous election to the National Inventors Hall of Fame in 1990. He was awarded honorary Doctor of Science degrees by Pennsylvania Military College in 1940 and by Grove City College in 1943. In 1967, the Catalysis Society of North America established the Houdry Award in Applied Catalysis.

Houdry died on July 18, 1962, at the age of 70, survived by his sons and his wife, Genevieve Quilleret. At that time he was actively working on creative ideas for using catalytic processes to improve human health.

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Further Reading

- [Eugene Houdry](#) (Chemical Heritage Foundation)

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Landmark Designation and Acknowledgments

Landmark Designation

The American Chemical Society designated the development of the Houdry process for catalytic cracking by Eugene Jules Houdry as a National Historic Chemical Landmark at the Marcus Hook Refinery of the Sun Company (now Sunoco Logistics Partners L.P.) in Marcus Hook, Pennsylvania, on April 13, 1996. The plaque commemorating the development reads:

The first full-scale commercial catalytic cracker for the selective conversion of crude petroleum to gasoline went on stream at the Marcus Hook Refinery. Pioneered by Eugene Jules Houdry (1892-1962), the catalytic cracking of petroleum revolutionized the industry. The Houdry process conserved natural oil by doubling the amount of gasoline produced by other processes. It also greatly improved the gasoline octane rating, making possible today's efficient, high-compression automobile engines. During World War II, the high-octane fuel shipped from Houdry plants played a critical role in the Allied victory. The Houdry laboratories in Linwood became the research and development center for this and subsequent Houdry inventions.

Acknowledgments

Adapted for the internet from "The Houdry Process," produced by the National Historic Chemical Landmarks program of the American Chemical Society in 1996.

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Sunoco officials pour the billionth gallon of aviation fuel produced during World War II.

Courtesy Sunoco Logistics/Sunoco, Inc.

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Chapter 1

PETROLEUM PROCESSING OVERVIEW

Paul R. Robinson

PQ Optimization Services, Inc.

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1. INTRODUCTION

The ground begins to rumble, then shake. The hero of the film – a lean ex-cowboy with a square jaw under his hat and a gorgeous brunette on his arm – reaches out to brace himself against his horse. A smile creases his face as the rumbling grows louder. Suddenly, a gush of black goo spurts into the air and splashes down on him, his side-kick and his best gal. They dance with ecstasy until the music swells and the credits start to roll.

Why is our hero so happy? Because he's rich! After years of drilling dry holes in every county between the Red River and the Rio Grande, he finally struck oil.

1.1 History of Petroleum Production

So why is he rich? What makes oil so valuable?

Actually, crude oil straight from the ground has some value, but not a lot. *Table 1* shows the history of petroleum before 1861. Before 1859, oil that was mined or that simply seeped up out of the ground was used to water-proof ships, as an adhesive in construction, for flaming projectiles, and in a wide variety of ointments.¹⁻⁴

After 1859, petroleum became more and more important to the world's economy, so important that today, without a steady flow of oil, most human activities on this planet would grind to a halt. Petroleum accounts for 60% of the world's shipping on a tonnage basis.³ It provides fuels and lubricants for our trucks, trains, airplanes, and automobiles. Ships are powered by fuel oil derived from petroleum. Bottom-of-the-barrel petroleum derivatives pave our roads and provide coke for the steel industry. Together with natural gas,

petroleum provides precursors for the world's petrochemical industries. At the end of 2003, the world was consuming 78 million barrels of oil per day.⁵ In August 2005, that volume of petroleum was worth \$4.6 billion per day, or \$1.7 trillion per year.

Table 1. History of Petroleum Before 1861

Date	Description
3000 BC	Sumerians use asphalt as an adhesive for making mosaics. Mesopotamians use bitumen to line water canals, seal boats, and build roads. Egyptians use pitch to grease chariot wheels, and asphalt to embalm mummies.
1500 BC	The Chinese use petroleum for lamps and for heating homes.
600 BC	Confucius writes about the drilling of 100-foot (30-meter) natural gas wells in China. The Chinese build pipelines for oil using bamboo poles.
600-500 BC	Arab and Persian chemists mix petroleum with quicklime to make Greek fire, the napalm of its day.
1200-1300 AD	The Persians mine seep oil near Baku (now in Azerbaijan).
1500-1600 AD	Seep oil from the Carpathian Mountains is used in Polish street lamps. The Chinese dig oil wells more than 2000 feet (600 meters) deep.
1735 AD	Oil is extracted from oil sands in Alsace, France.
Early 1800s	Oil is produced in United States from brine wells in Pennsylvania.
1847	James Oakes builds a "rock oil" refinery in Jacksdale, England. ⁶ The unit processes 300 gallons per day to make "paraffin oil" for lamps. James Young builds a coal-oil refinery in Whitburn, Scotland. ⁷
1848	F.N. Semyenov drills the first "modern" oil well near Baku.
1849	Canadian geologist Abraham Gesner distills kerosene from crude oil.
1854	Ignacy Lukasiewicz drills oil wells up to 150 feet (50 meters) deep at Bóbrka, Poland.
1857	Michael Dietz invents a flat-wick kerosene lamp (Patent issued in 1859). ⁸
1858	Ignacy Lukasiewicz builds a crude oil distillery in Ulaszowice, Poland. ⁸ The first oil well in North America is drilled near Petrolia, Ontario, Canada.
1859	Colonel Edwin L. Drake triggers the Pennsylvania oil boom by drilling a well near Titusville, Pennsylvania that was 69-feet deep and produced 35 barrels-per-day.
1859	An oil refinery is built in Baku (now in Azerbaijan).
1860-61	Oil refineries are built near Oil Creek, Pennsylvania; Petrolia, Ontario, Canada; and Union County, Arkansas.

So what happened in 1859? What began the transformation of petroleum from a convenience into the world's primary source of energy? As often is the case with major socioeconomic shifts, the move toward oil was instigated not by just a single event, but by the juxtaposition of several:

- In the 1850s, most home-based lamps burned whale oil or other animal fats. Historically, whale-oil prices had always fluctuated wildly, but they peaked in the mid-1850s due to the over-hunting of whales; by some estimates, in 1860 several species were almost extinct. Whale oil sold for an average price of US\$1.77 per gallon between 1845 and 1855. In contrast, lard oil sold for about US\$0.90 per gallon.^{9,10} Lard oil was more abundant, but it burned with a smoky, smelly flame.

- Michael Dietz invented a flat-wick kerosene lamp in 1857. The Dietz lamp was arguably the most successful of several devices designed to burn something other than animal fats.
- The availability of kerosene got a sudden boost on August 27, 1859, when Edwin L. Drake struck oil with the well he was drilling near Titusville, Pennsylvania. By today's standards, the well was shallow – about 69 feet (21 meters) deep and it produced only 35 barrels per day. Drake was able to sell the oil for US\$20 per barrel, a little less than the price of lard oil and 70% less than the price of whale oil. In 1861, US\$700 per day was a tidy sum, equivalent to US\$5 million per year in 2002 dollars.¹¹ Drake's oil well was not the first – according to one source, the Chinese beat Drake by about 2200 years – but it may have been the first drilled through rock, and it certainly triggered the Pennsylvania oil rush. Figure 1 shows some of the closely spaced wells that sprang up in 1859 in the Pioneer Run oil field a few miles from Titusville.



Figure 1. Pioneer Run oil field in 1859. Photo used with permission from the Pennsylvania Historical Collection and Museum Commission, Drake Well Museum Collection, Titusville, PA.

According to a report issued in 1860 by David Dale Owens,¹² the state geologist of Arkansas:

“On Oil Creek in the vicinity of Titusville, Pennsylvania, oil flows out from some wells at the rate of 75 to 100 gallons in 24 hours already fit for the market. At least 2000 wells are now in progress and 200 of these are already pumping oil or have found it.”

According to *The Prize*,¹³ a prize-winning book by Daniel Yergin:

“When oil first started flowing out of the wells in western Pennsylvania in the 1860’s, desperate oil men ransacked farmhouses, barns, cellars, stores, and trash yards for any kind of barrel – molasses, beer, whiskey, cider, turpentine, sale, fish, and whatever else was handy. But as coopers began to make barrels especially for the oil trade, one standard size emerged, and that size continues to be the norm to the present. It is 42 gallons.

“The number was borrowed from England, where a statute in 1482 under King Edward IV established 42 gallons as the standard size barrel for herring in order to end skullduggery and “divers deceits” in the packing of fish. At the time, herring fishing was the biggest business in the North Sea. By 1866, seven years after Colonel Drake drilled his well, Pennsylvania producers confirmed the 42-gallon barrel as their standard, as opposed to, say, the 31½ gallon wine barrel or the 32 gallon London ale barrel or the 36 gallon London beer barrel.”

In sharp contrast to the situation today, in 1870 America was the world’s leading oil producer, and oil was America’s 2nd biggest export.⁴ Agricultural products were first, accounting for 79% of exports that were worth, on average, US\$573 million per year from 1870 to 1879.¹⁴ Despite the ravages of the U.S. Civil War, the main agricultural export was still “King Cotton.”

1.2 What Is Petroleum?

Before we go on to talk about petroleum processing, it is important to know something about petroleum itself. Petroleum is called a fossil fuel because it is formed from the bodies of ancient organisms – primarily one-celled plants and animals (see Chapter 2). Contrary to modern myth, only a tiny fraction (if any) of the molecules in crude oil are from dinosaurs. When these creatures died, their remains accumulated at bottoms of ancient lakes or seas, along with sand and other sediments. Over time, a combination of pressure, heat, and bacterial action transformed the deposits into sedimentary rock. The incorporated organic matter was transformed into simpler chemicals, such as hydrocarbons, water, carbon dioxide, hydrogen sulfide, and others.

The chemicals didn’t always stay put. If the surrounding rock was porous, liquids and gases could migrate, either up to the surface or into a reservoir (*Figure 2*) that was capped by impermeable rock or a dome of salt. Today, when petroleum geologists look for oil, they actually are looking for structures that might be traps for liquid hydrocarbons.

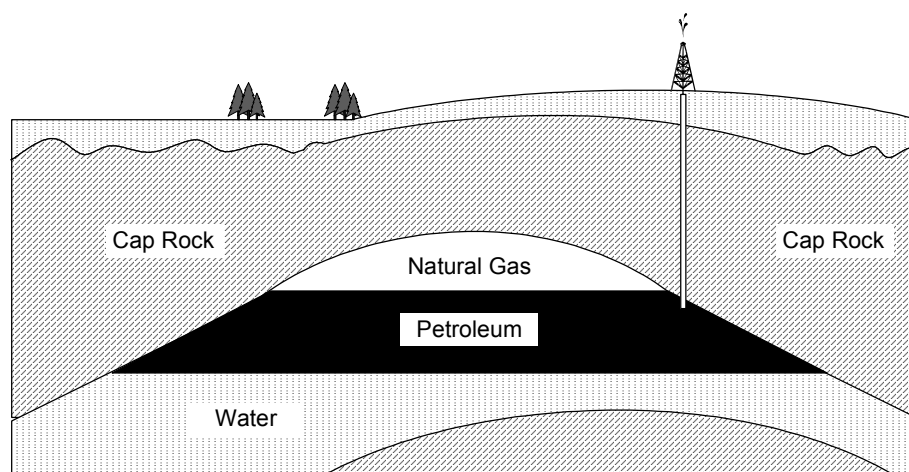


Figure 2. Petroleum Reservoir

In solid sources of fossil fuel – coal, oil shale, oil sands and tar sands – the mineral content is higher and the hydrocarbon molecules usually are heavier. In China and South Africa, a significant amount of coal is converted into synthesis gas, which is used to make chemicals and/or synthetic petroleum. In Canada, oil sands are converted into more than 700,000 barrels-per-day of synthetic petroleum, which is sent to conventional oil refineries in Canada and the United States. A well-written book by Berger and Anderson¹⁵ provides additional general information about the formation, production, and refining of petroleum.

Due to its origin, crude oil is a complex mixture containing thousands of different hydrocarbons.^{16,17} As the name implies, hydrocarbons are chemicals containing hydrogen and carbon. In addition to hydrogen and carbon, most crude oils also contain 1 to 3 wt% sulfur along with smaller amounts of nitrogen, oxygen, metals, and salts. The salts can be removed with a hot-water wash (see Section 2), but the other major contaminants – sulfur, nitrogen, oxygen and metals – are harder to remove because they are linked to hydrocarbons by chemical bonds.

Crude oils from some wells are as clear as vegetable oil. Other wells produce green, brown or black crudes. Some taste sour or smell like rotten eggs. Some flow as easily as water, others don't flow unless they are heated, and some are so solid they have to be mined.

Table 2 compares properties for 21 selected crudes. Traders characterize a crude by citing its source, API gravity (a measure of density), and sulfur content. The source is the oil field from which the crude was produced. The API gravity is a rough indication of distillation properties, which determine how much gasoline, kerosene, etc., can be distilled from the crude. Along with other factors, the sulfur content affects processing costs. Figure 3 shows

that light crudes (those with high API gravities) often contain less sulfur and nitrogen than heavy crudes, but not always.

Table 2. Properties of 21 Selected Crude Oils

Crude Oil	API Gravity [†]	Specific Gravity	Sulfur (wt%)	Nitrogen (wt%)
Alaska North Slope	26.2	0.8973	1.1	0.2
Arabian Light	33.8	0.8560	1.8	0.07
Arabian Medium	30.4	0.8740	2.6	0.09
Arabian Heavy	28.0	0.8871	2.8	0.15
Athabasca (Canada)	8	1.0143	4.8	0.4
Beta (California)	16.2	0.9580	3.6	0.81
Brent (North Sea)	38.3	0.8333	0.37	0.10
Bonny Light (Nigeria)	35.4	0.8478	0.14	0.10
Boscan (Venezuela)	10.2	0.9986	5.3	0.65
Ekofisk (Norway)	37.7	0.8363	0.25	0.10
Henan (China)	16.4	0.9567	0.32	0.74
Hondo Blend (California)	20.8	0.9291	4.3	0.62
Kern (California)	13.6	0.9752	1.1	0.7
Kuwait Export	31.4	0.8686	2.5	0.21
Liaohi (China)	17.9	0.9471	0.26	0.41
Maya (Mexico)	22.2	0.9206	3.4	0.32
Shengli (China)	13.8	0.9738	0.82	0.72
Tapis Blend (Malaysia)	45.9	0.7976	0.03	nil
West Hackberry Sweet*	37.3	0.8383	0.32	0.10
West Texas Intermediate	39.6	0.8270	0.34	0.08
Xinjiang (China)	20.5	0.9309	0.15	0.35

* Produced from a storage cavern in the U.S. Strategic Petroleum Reserve

[†] **API Gravity** is related to specific gravity by the formula:

$$^{\circ}\text{API} = 141.5 \div (\text{specific gravity @ } 60^{\circ}\text{F}) - 131.5$$

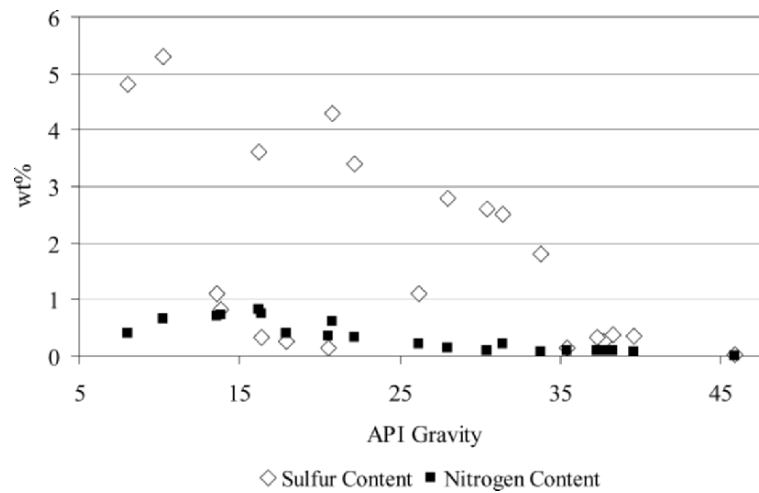


Figure 3. Sulfur and nitrogen versus API gravity for selected crude oils

1.2.1 The Chemicals in Petroleum

Carbon is present in almost all of the chemical compounds in petroleum. If you've ever taken a chemistry class, you know that carbon, more than any other element, binds to itself to form straight chains, branched chains, rings, and complex three-dimensional structures. The most complex molecules are biological – proteins, carbohydrates, fats and nucleic acids, which are present in every living thing, from the smallest bacterium to the largest tree. This is significant here because (as stated above) petroleum was formed from ancient organisms, and its molecules retain certain structural characteristics of the organic compounds from which it formed.

1.2.1.1 Paraffins

The lightest paraffin is methane (CH_4) which is the major constituent of natural gas. Paraffins have the general formula $\text{C}_n\text{H}_{2n+2}$. The carbon chains in paraffins can be straight or branched. Compounds with the same formula but different structures are called isomers. Straight-chain paraffins are “normal,” while branched paraffins with the same chemical formula are called “iso.”

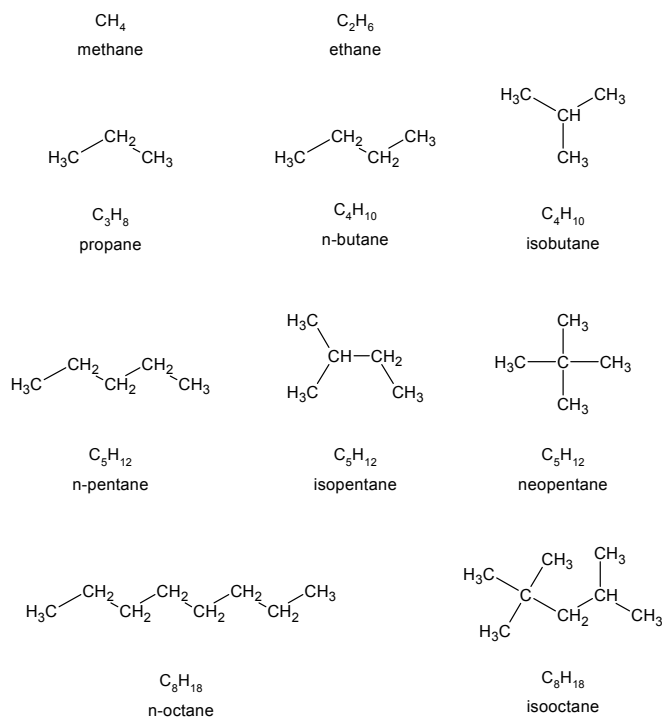


Figure 4. Isomers of selected light paraffins

Tables 3 and 4 show that isomers have different physical properties.¹⁸ They also can have significantly different chemical properties. For gasoline, one of the most important chemical properties is octane number. The research octane number (RON) for n-octane is -27 compared to a RON of 100 (by definition) for isooctane (2,2,3-trimethylpentane). For heptane isomers, RON values range from 45 for 2-methyl-hexane to >100 for 2,2,3-trimethylbutane, compared to zero (by definition) for n-heptane. Octane numbers are discussed in more detail in Section 8.2.

Table 3. Boiling Points of Selected Light Paraffins

Name	Formula	Boiling Point (°F)	Boiling Point (°C)
Methane	CH ₄	-259.9	-162.2
Ethane	C ₂ H ₆	-127.4	-88.6
Propane	C ₃ H ₈	-43.7	-42.1
n-Butane	C ₄ H ₁₀	31.7	-0.1
Isobutane	C ₄ H ₁₀	11.9	-11.2
n-Pentane	C ₅ H ₁₂	96.9	36.1
Isopentane	C ₅ H ₁₂	82.3	28.0
Neopentane	C ₅ H ₁₂	49.0	9.5
n-Octane	C ₈ H ₁₈	258.0	125.6
Isooctane	C ₈ H ₁₈	210.7	99.3

The melting points of paraffin isomers also can differ significantly. As shown in Table 5, long-chain n-paraffins melt at relatively high temperatures, while their branched-chain isomers melt at lower temperatures. This explains their different behaviours as lubricants. Long-chain normal paraffins are waxy, so as lubricants they are terrible. Conversely, iso-paraffins with the same number of carbons are excellent lube base stocks.

Table 4. Fusion Points for Selected C₁₆ Paraffins.

Name	Formula	Melting Point (°F)	Melting Point (°C)
Hexadecane	C ₁₆ H ₃₄	64.1	17.9
5-Methylpentadecane	C ₁₆ H ₃₄	-29.5	-34.2
7,8-Dimethyltetradecane	C ₁₆ H ₃₄	-123.1	-86.2

1.2.1.2 Aromatics and Naphthenes

Aromatics and naphthenes are also found in petroleum. Aromatics contain one or more unsaturated 5 to 6-carbon rings. In naphthenes, carbon rings are saturated with hydrogen.

Figure 5 shows structures for a few of the aromatics and naphthenes that have been found in crude oils. For aromatics with one six-carbon ring, the general formula is C_nH_{2n-6}, and for naphthenes with one ring, the general formula is C_nH_{2n}.

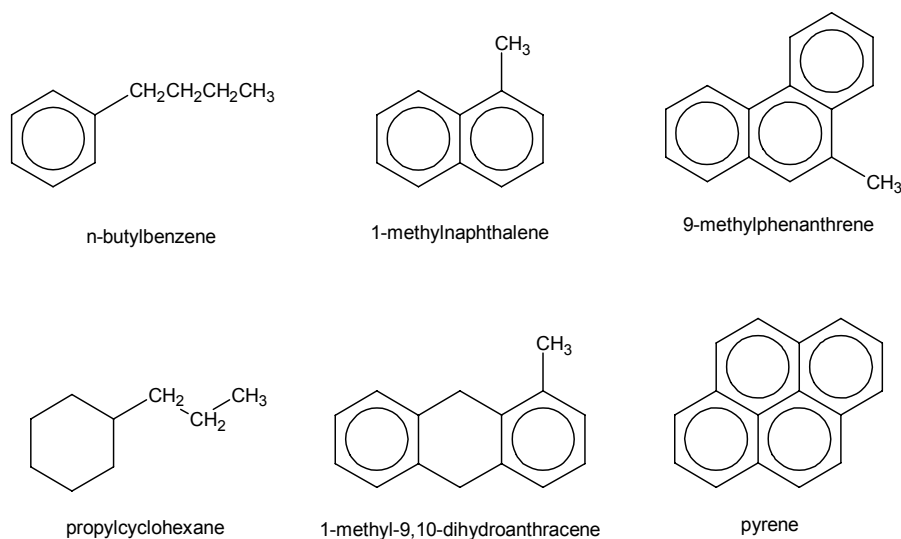


Figure 5. Aromatics and naphthenes found in crude oil

Aromatics and naphthenes display significantly different chemical and physical properties. Compared to paraffins and naphthenes with the same carbon number, aromatics are denser and have higher octane numbers.

1.2.1.3 Hetero-atom Compounds

When present in organic compounds, atoms other than carbon and hydrogen are called hetero-atoms. As mentioned above, sulfur, nitrogen, oxygen and metals are minor constituents of crude oil, but as we shall see, their impact on processing costs can be major. *Figure 6* shows some of the sulfur and nitrogen compounds that present problems to oil refiners. When burned in vehicles or power plants, high-sulfur fuels cause acid rain. For many refining processes, sulfur is a catalyst poison. Nitrogen and metals also are catalyst poisons. Therefore, refiners devote a considerable amount of time and money to remove hetero-atoms from intermediate streams and finished products.

1.2.1.4 Olefins

We need to discuss one more class of molecules before moving on. Due to their high reactivity, olefins are not common in natural crude oil. However, in refineries they are generated by several “cracking” processes. *Figure 7* shows structures for some common light olefins.

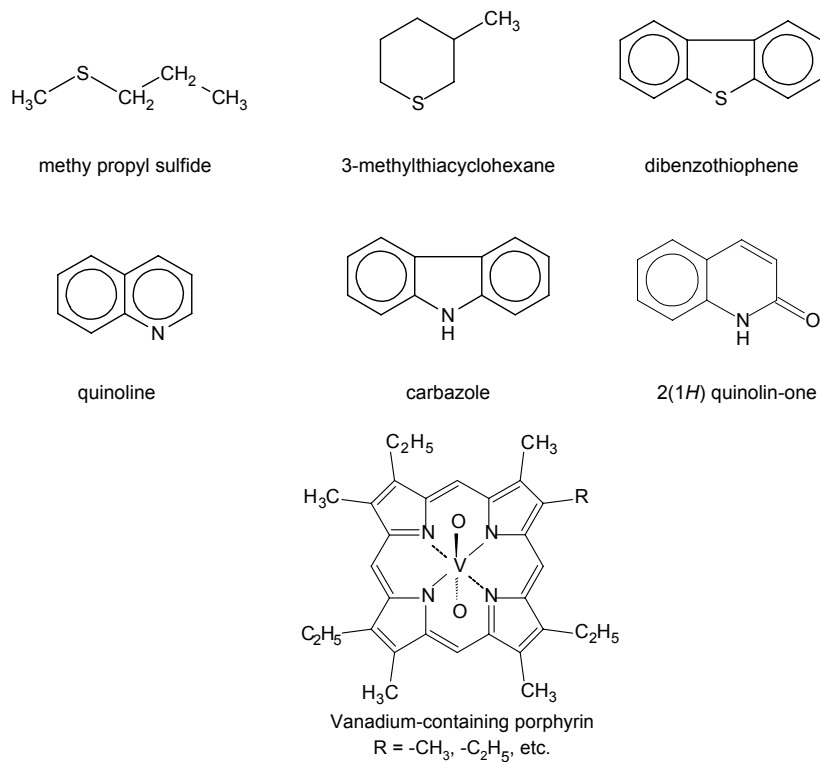


Figure 6. Hetero-atom compounds found in crude oil

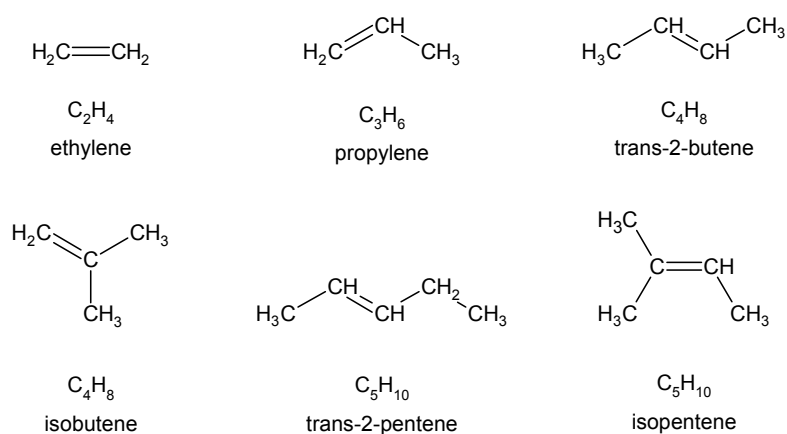


Figure 7. Selected light olefins

1.3 History of Petroleum Processing

These days, it's extremely rare for oil to flow out of a well already fit for the market as it did in the 1860s near Oil Creek, Pennsylvania.¹² Crudes from the Tapis field in Malaysia are almost good enough for direct use in diesel engines, but even these high-quality "boutique crudes" are sent to refineries for separation into higher-value components.

As mentioned in Section 1.1, in the 1860s the most valuable crude-oil fraction was kerosene. From the first crude distillation units – which truly were crude, comprising cast-iron kettles, water-cooled coils and wooden product-collection vats – part of the lightest fraction (naphtha) was sold as a solvent, but most of it was burned off. Distillates heavier than kerosene (gas oils) found some use as lubricants, but the undistilled residues were discarded.

1.3.1 Demand for Conversion

The demand for petroleum remained relatively flat throughout the last half of the 19th Century. In 1878, thanks to the inventions of Thomas Edison, electric lighting slowly but surely began to displace kerosene as a preferred illuminant. (*Table 5*)

But the biggest blow to kerosene came from the gasoline-powered automobile. Developed in 1889 by Gottlieb Daimler, Wilhelm Maybach, and (separately) by Karl Benz, the motor car was a curiosity until 1901, when Ransom Eli Olds started assembly-line production of the Curved Dash Oldsmobile Runabout.¹⁹

Henry Ford built his first gasoline-powered car in 1896 and founded the Ford Motor Company in 1903. In 1908 he began selling Model T's for the low, low price of US\$950. The resulting boom in automobile sales triggered tremendous growth in petroleum demand, which continued unabated until the Arab Oil Embargo of 1973. Over 15 million Model T Fords were sold in the United States alone between 1908 and 1917, with prices as low as US\$280 per unit.¹⁹

In addition to increasing the overall demand for petroleum, the advent of the automobile increased the relative demand for naphtha (from which gasoline is derived) versus kerosene. In response, refiners developed conversion processes. The first of these was the thermal cracking process patented by William Burton and Robert Humphreys, who were working for Standard Oil of Indiana. The Burton-Humphreys process doubled the yield of gasoline from crude oil, and it is credited for averting a gasoline shortage during World War I. Moreover, gasoline from thermal crackers performed better in automobiles than straight-run products distilled from crude petroleum.

Table 5. Significant Events in Petroleum Processing, 1861 – 2000

Date	Description
1878	Thomas Edison invents the light bulb. The use of kerosene lamps starts to decline.
1889	Gottlieb Daimler, Wilhelm Mayback and (separately) Karl Benz build gasoline-powered automobiles.
1901	Ransom E. Olds begins assembly-line production of the Curved Dash Oldsmobile.
1908	Ford Motor Company offers Model T's for US\$950 each.
1912	William Burton and Robert Humphreys develop thermal cracking.
1913	Gulf Oil builds the world's first drive-in filling station in Pittsburgh, Pennsylvania.
1919	UOP commercializes the Dubbs thermal cracking process.
1929	Standard Oil of Indiana (now BP) commercializes the Burton process for delayed coking at Whiting, Indiana.
1933	UOP introduces the catalytic polymerization of olefins to form gasoline.
1934	Eugene Houdry, working for Sun Oil, patents Houdry Catalytic Cracking (HCC).
1938	A consortium of refiners develops sulfuric acid alkylation, which is first commercialized at the Humble (now ExxonMobil) refinery in Baytown, Texas.
1940	Phillips develops HF alkylation.
1942	Standard Oil of New Jersey (now ExxonMobil) commercializes the FCC process at Baton Rouge, Louisiana.
1949	Old Dutch Refining in Muskegon, Michigan starts the world's first catalytic reformer based on the UOP Platforming processes.
1950	Catalytic hydrotreating is patented by Raymond Fleck and Paul Nahin of Union Oil.
1960s	UOP introduces C ₄ and C ₅ /C ₆ isomerization processes.
1961	Standard Oil of California (now Chevron) introduces catalytic hydrocracking.
1970	The world celebrates Earth Day. The newly created U.S. Environmental Protection Agency passes the Clean Air Act, which requires a 90% reduction in auto emissions by 1975. The European Union issues similar requirements.
1972	Mobil invents ZSM-5. During the next three decades, this shape-selective catalyst finds uses in numerous processes, including FCC, catalytic dewaxing, and the conversion of methanol to gasoline.
1975	The catalytic converter goes commercial. The phase-out of tetraethyl lead begins.
1990	The U.S. Congress issues the Clean Air Act Amendments of 1990, which lay the framework for reformulated gasoline and low-sulfur diesel.
1990s	Several processes are developed to remove sulfur from gasoline. These include SCANfining (Exxon), OCTGAIN (Mobil), Prime G (Axens), and S Zorb (Phillips).
1993	Chevron commercializes Isodewaxing for converting waxy paraffins into high-quality lube base stock.
2000	The European Commission issues the Auto Oil II report, which includes a timetable for low-sulfur gasoline and ultra-low-sulfur diesel.

In 1914, Jesse A. Dubbs and J. Ogden Armour founded the National Hydrocarbon Company, which later became Universal Oil Products (UOP).²⁰ UOP grew to become the world's largest licensor of process technology for the oil refining industry. In 1919, UOP commercialized the Dubbs process, which solved some of the problems associated with the Burton-Humphreys process. The Dubbs process produced fewer coke deposits, it could process heavier petroleum fractions, and it ran longer between shutdowns.

Standard Oil of Indiana commercialized the delayed coking process at Whiting, Indiana in 1929. In 1933, UOP commercialized the conversion of olefins to gasoline via catalytic polymerization. Later in the 1930s, refiners began using tetraethyl lead to boost the octane of gasoline. A consortium of

refining companies – Anglo-Iranian, Humble, Shell Oil, Standard Oil, and Texaco – developed sulfuric acid alkylation, which was commercialized in 1938 at the Humble (now ExxonMobil) refinery in Baytown, Texas. In 1940, Phillips Petroleum (now ConocoPhillips) developed HF alkylation.

Eugene Houdry patented the Houdry Catalytic Cracking (HCC) process in 1934. HCC was commercialized in 1937. With amazing foresight, Houdry also invented the catalytic converter, which started appearing on automobiles in the 1970s.

In 1942, Standard Oil of New Jersey (now ExxonMobil) commercialized the fluidized catalytic cracking (FCC) process, which dramatically increased a refiner's ability to convert heavy gas oils into gasoline. The four inventors of this process, which still produces more than half of the world's gasoline, were Donald L. Campbell, Homer Z. Martin, Eger V. Murphree, and Charles W. Tyson. During 1942-45, several FCC-based refineries were built in the United States to produce automotive and aviation gasoline during World War II.

After 1945, the development of new refining processes was stimulated by a continuing increase in demand for petroleum products, coupled with the increased availability of oil from the Middle East and elsewhere. The quality of gasoline got a large boost from catalytic reforming, which first appeared in 1949 at the Old Dutch refinery in Muskegon, Michigan. The unit was based on technology developed by UOP, which employed a platinum-based catalyst invented by Vladimir N. Ipatieff.

In 1961, hydrocracking was introduced to convert gas oil into naphthene-rich heavy naphtha, which is a superb feed for a catalytic reformer. The first unit used the Isocracking process developed by Standard Oil of California (now Chevron Texaco).

1.3.2 Demand for a Clean Environment

In 1970, President Richard M. Nixon established the U.S. Environmental Protection Agency (EPA) and the U.S. Congress passed the Clean Air Act (CAA). The CAA required a 90% reduction in auto emissions by 1975. The scope and timing of this requirement presented a challenge to the automobile industry.²¹ After reviewing several alternatives, auto makers focused on developing catalytic converters to remove carbon monoxide and hydrocarbons from automobile exhaust. Also in 1970, the European Union issued directive 70/220/EEC, which specified similar emission limits for passenger cars.

Lead poisons the active metal (platinum) in catalytic converters, so in 1975 EPA promulgated a phase-out plan to remove lead from gasoline.

In the 1990s and 2000s, the California Air Resources Board (CARB), the U.S. EPA and the European Commission promulgated requirements for reformulated gasoline, low-sulfur diesel, low-sulfur gasoline and ultra-low-sulfur diesel (ULSD). ULSD will enable the use of advanced emission

controls (including catalytic converters) on diesel-powered cars and trucks. Refiners are responding by installing additional hydrotreating capacity.

1.4 Modern Petroleum Processing

All refineries are different. They have different histories, locations, and market drivers. Therefore, no single illustration can capture all of the possible combinations and permutations of the processes that fit together to comprise an oil refinery. But despite their differences, most refineries perform the seven basic operations named in *Table 6*.

Table 6. Seven Basic Operations in Petroleum Processing

Separation	Combination
<ul style="list-style-type: none"> • Distillation • Solvent refining 	<ul style="list-style-type: none"> • Catalytic polymerization • Alkylation
Conversion	Treating, finishing, blending
<ul style="list-style-type: none"> • Carbon removal • Hydrogen addition 	<ul style="list-style-type: none"> • Gasoline, kerosene and diesel • Lubes and waxes • Asphalt
Reforming	Protecting the Environment
<ul style="list-style-type: none"> • Catalytic reforming • Steam/hydrocarbon reforming 	<ul style="list-style-type: none"> • Waste water treatment • Disposal of solids • Sulfur recovery
Rearrangement	
<ul style="list-style-type: none"> • Isomerization 	

Figure 8 shows a simplified layout for a high-conversion refinery in the United States. The diagram doesn't show product blending and sulfur recovery units, but these are almost always present. Lube-oil processing and hydrogen production units also may be present.

The depicted plant is configured for maximum fuels production. In a typical European refinery, the coker would be replaced with a visbreaker. In many Asian refineries, where diesel demand is higher than gasoline demand, the coker would be replaced by a visbreaker and the FCC by a hydrocacker.

The rest of this chapter provides a brief overview of the processes shown or mentioned above. The chapters that follow provide detailed process descriptions, with emphasis on recent developments. General information on refining technology can be found in the excellent books by E.I. Shaheen,²² and W.L. Leffler,²³ and in a manual published by the U.S. Occupational Safety and Health Administration.²⁴ Each year, *Hydrocarbon Processing* compiles a widely read refining process handbook, which gives descriptions of about 120 licensed processes offered by engineering contractors, oil companies, and of course process licensors.²⁵

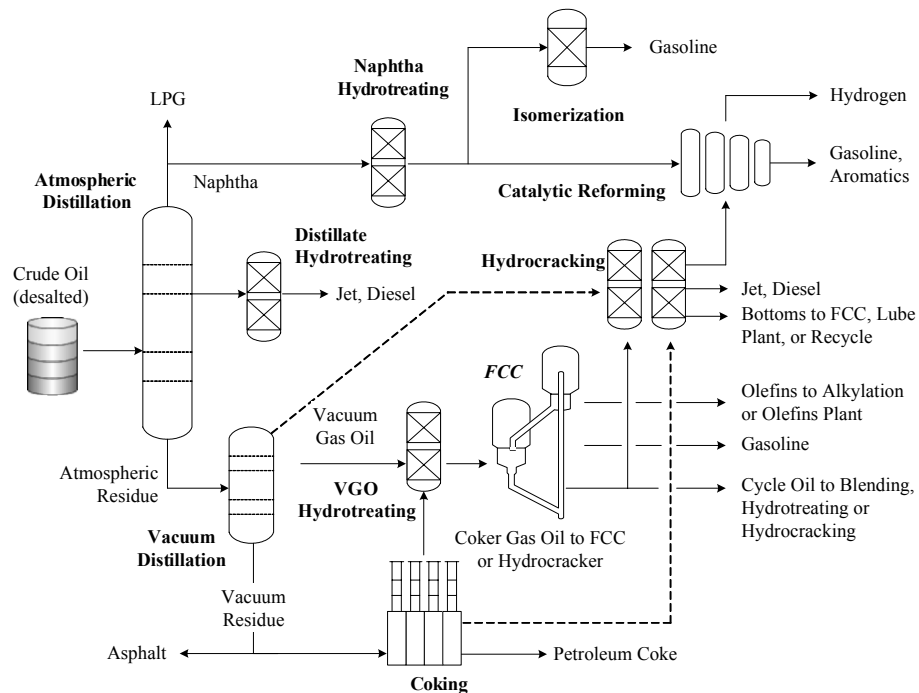


Figure 8. Typical layout for an oil refinery

2. SEPARATION

2.1 Distillation

In terms of throughput, the biggest unit in most plants is the crude distillation unit (*Figure 9*). Many downstream conversion units also use distillation for production separation. For example, in a coker, hydrocracker, or FCC unit, an atmospheric tower, a vacuum tower, and a multi-column gas plant may be required.

2.1.1 Atmospheric Distillation

Crude oil distillation is more complicated than product distillation, in part because crude oils contain water, salts, and suspended solids. To reduce corrosion, plugging, and fouling in crude heaters and towers, and to prevent the poisoning of catalysts in downstream units, these contaminants are removed by a process called desalting.

The two most typical methods of crude-oil desalting – chemical and electrostatic separation – use hot water to dissolve the salts and collect

suspended solids. In chemical desalting, water and surfactants are added to the crude, heated to dissolve salts and other impurities, and then sent to a settling tank where the water and oil separate. In electrostatic desalting, chemicals are replaced with a strong electrostatic charge, which drives the separation of water from oil.

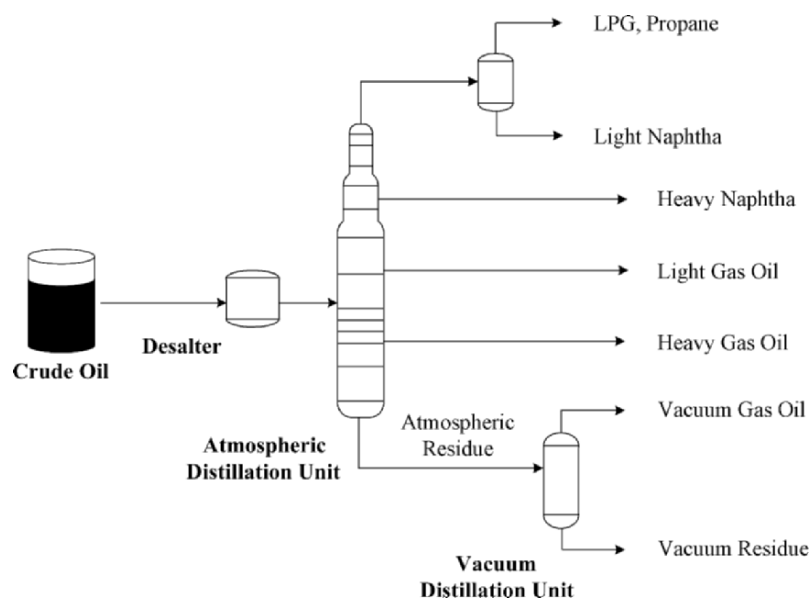


Figure 9. Crude distillation

Modern crude distillation towers can process 200,000 barrels of oil per day. They can be up to 150 feet (50 meters) tall and contain 20 to 40 fractionation trays spaced at regular intervals. In some towers, the trays in the top section are replaced with structured packing.

Before reaching the tower, desalted oil goes through a network of pre-heat exchangers to a fired heater, which brings the temperature up to about 650°F (343°C). If the oil gets much hotter than this, it starts to crack and deposit carbon inside the pipes and equipment through which it flows. The hot crude enters the distillation tower just above the bottom. Steam is added to enhance separation; it does so largely by decreasing vapor pressure in the column.

When hot oil enters the tower, most of it vaporizes. Unvaporized heavy fuel oil and/or asphalt residue drops to the bottom of the tower, where it is drawn off. The vapors rise through the distillation trays, which contain perforations and bubble caps (Figure 10). Each tray permits vapors from below to bubble through the cooler, condensed liquid on top of the tray. This

provides excellent vapor/liquid contacting. Condensed liquid flows down through a pipe to the hotter tray below, where the higher temperature causes re-evaporation. A given molecule evaporates and condenses many times before finally leaving the tower.

Products are collected from the top, bottom and side of the column. Side-draw products are taken from trays at which the temperature corresponds to the cutpoint for a desired product. In modern towers, a portion of each side-draw stream is returned to the tower to control tray temperatures and further enhance separation. Part of the top product is also returned; this “reflux” flow plays a major role in controlling temperature at the top of the tower.

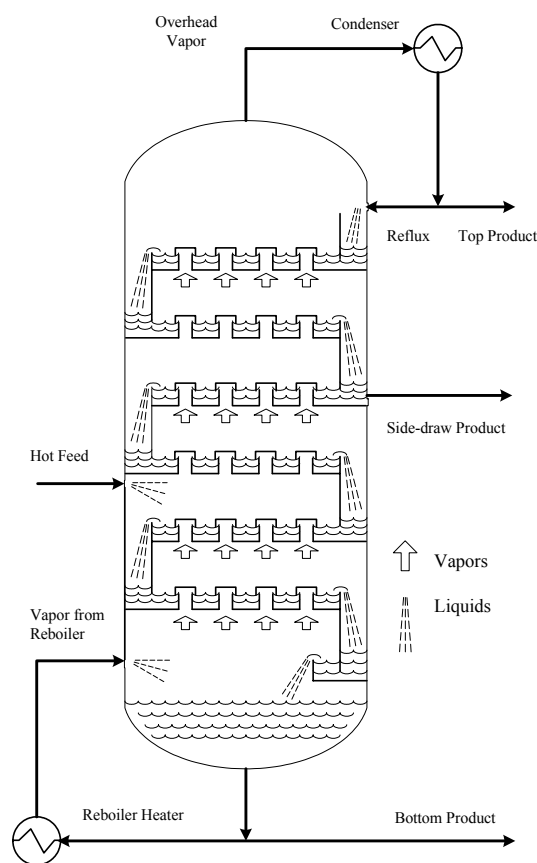


Figure 10. Distillation column with bubble-cap trays

After leaving the tower, product streams go to holding tanks or directly to downstream process units. As shown in *Figure 9* and *Table 7*, products can include heavy fuel oil, heating oil, kerosene, gasoline, and uncondensed gases.

Table 7. Destinations for Straight-Run Distillates

Fraction	Approx. Boiling Range		Next Destination	Ultimate Product(s)
	°C	°F		
LPG	-40 to 0	-40 to 31	Sweetener	Propane fuel
Light Naphtha	39 - 85	80 - 185	Hydrotreater	Gasoline
Heavy Naphtha	85 - 200	185 - 390	Cat. Reformer	Gasoline, aromatics
Kerosene	170 - 270	340 - 515	Hydrotreater	Jet fuel, No. 1 diesel
Gas Oil	180 - 340	350 - 650	Hydrotreater	Heating Oil, No. 2 diesel
Vacuum Gas Oil	340 - 566	650 - 1050	FCC	Gasoline, LCO, gases
			Hydrotreater	Fuel oil, FCC feed
			Lube Plant	Lube basestock
			Hydrocracker	Gasoline, jet, diesel, FCC feed, lube basestock
Vacuum Residue	>540	>1000	Coker	Coke, coker gas oil
			Visbreaker	Visbreaker gas oil, resid
			Asphalt Unit	Deasphalted oil, asphalt
			Hydrotreater	FCC feed

Table 8 shows that straight-run yields from various crude oils can differ substantially. The naphtha content of Brent is twice as high as Ratawi, and its vacuum residue content is 60% lower. Bonny Light yields the most middle distillate and the least vacuum residue.

Table 8. Typical Straight-run Yields from Various Crudes^{26,27}

Source field	Brent	Bonny Lt.	Green Canyon	Ratawi
Country	Norway	Nigeria	USA	Mid East
API gravity	38.3	35.4	30.1	24.6
Specific gravity	0.8333	0.8478	0.8752	0.9065
Sulfur, wt%	0.37	0.14	2.00	3.90
Yields, wt% feed				
Light ends	2.3	1.5	1.5	1.1
Light naphtha	6.3	3.9	2.8	2.8
Medium naphtha	14.4	14.4	8.5	8.0
Heavy naphtha	9.4	9.4	5.6	5.0
Kerosene	9.9	12.5	8.5	7.4
Atmospheric gas oil	15.1	21.6	14.1	10.6
Light VGO	17.6	20.7	18.3	17.2
Heavy VGO	12.7	10.5	14.6	15.0
Vacuum residue	12.3	5.5	26.1	32.9
Total naphtha	30.1	27.7	16.9	15.8
Total middle distillate	25.0	34.1	22.6	18.0

Atmospheric distillation of the best crudes yields about 60% naphtha plus middle distillates (kerosene and gas oil), but the average is closer to 40%. In contrast, Table 9 shows that during 1991-2003, the United States consumed, on average, 70% of its petroleum as gasoline and middle distillates. This

leaves a gap of about 30%, which is satisfied by converting residual oils into lighter products (Section 3).

Table 9. Average U.S. Consumption of Petroleum Products, 1991-2003²⁸

Product	Consumption (barrels/day)	Percent of Total
Gasoline	8,032	43.6%
Jet Fuel	1,576	8.6%
Total Distillates	3,440	18.7%
Residual Fuel Oil	867	4.8%
Other Oils	4,501	24.4%
Total Consumption	18,416	100%
Sum of Gasoline, Jet, Distillates	13,048	70.8%

2.1.2 Vacuum Distillation

The residue from an atmospheric distillation tower can be sent to a vacuum distillation tower, which recovers additional liquid at 0.7 to 1.5 psia (4.8 to 10.3 kPa). The vacuum, which is created by a vacuum pump or steam ejector, is pulled from the top of the tower. Relative to atmospheric columns, vacuum columns have larger diameters and their internals are simpler. Often, instead of trays, random packing and demister pads are used.

The overhead stream – light vacuum gas oil – can be used as a lube base stock, heavy fuel oil, or as feed to a conversion unit. Heavy vacuum gas oil is pulled from a side draw. The vacuum residue can be used to make asphalt, or it can be sent to a coker or visbreaker unit for further processing.

2.2 Solvent Refining

Distillation splits a mixture into fractions according to the boiling points of the mixture constituents. In contrast, solvent refining segregates compounds with similar compound types, such as paraffins and aromatics. The three main types of solvent refining are solvent deasphalting, solvent extraction, and solvent dewaxing.

2.2.1 Solvent Deasphalting

Solvent deasphalting takes advantage of the fact that aromatic compounds are insoluble in paraffins. Propane deasphalting is commonly used to precipitate asphaltenes from residual oils. Deasphalted oil (DAO) is sent to hydrotreaters, FCC units, hydrocrackers, or fuel-oil blending. In hydrocrackers and FCC units, DAO is easier to process than straight-run residual oils. This is because asphaltenes easily form coke and often contain catalyst poisons such as nickel and vanadium, and the asphaltene content of DAO is (by definition) almost zero.

In traditional solvent deasphalting, residual oil and propane are pumped to an extraction tower at 150 to 250°F (65 to 120°C) and 350 to 600 psig (2514 to 4240 kPa). Separation occurs in a tower, which may have a rotating disc contactor (*Figure 11*). Liquid products are evaporated and steam stripped to recover the propane solvent, which is recycled.

An advanced version of solvent deasphalting is “residuum oil supercritical extraction,” or ROSE. The ROSETM Process was developed by the Kerr-McGee Corporation and now is offered for license by KBR Engineering and Construction, a subsidiary of Halliburton. In this process, the oil and solvent are mixed and heated to above the critical temperature of the solvent, where the oil is almost totally insoluble. Advantages include higher recovery of deasphalted liquids, lower operating costs due to improved solvent recovery, and improved energy efficiency. The ROSE process can employ three different solvents, the choice of which depends upon process objectives:

Propane:	Preparation of lube base stocks
Butane:	Asphalt production
Pentane:	Maximum recovery of liquid

2.2.2 Solvent Extraction

Solvent extraction is used to remove aromatics and other impurities from lube and grease stocks. The feedstock is dried, then contacted with the solvent in a counter-current or rotating disk extraction unit (*Figure 11*). The solvent is separated from the product stream by heating, evaporation, or fractionation. Remaining traces of solvent are removed from the raffinate by steam stripping or flashing. Electrostatic precipitators may be used to enhance separation of inorganic compounds. The solvent is then regenerated and recycled.

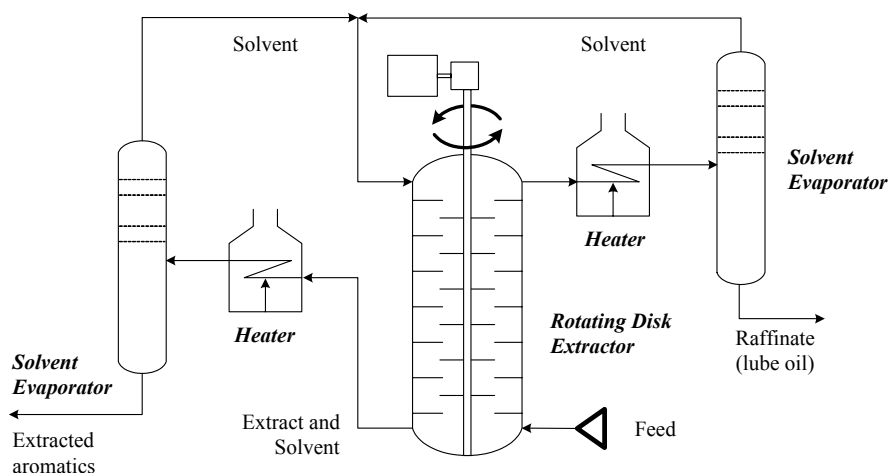


Figure 11. Rotating-disk solvent extraction

Today, phenol, furfural, and cresylic acid are widely used as solvents. In the past, some refiners installed the Edeleanu process, in which the solvent is liquid sulfur dioxide, but the hazards of potential leaks made it undesirable. Chlorinated ethers and nitrobenzene also have been used.

2.2.3 Solvent Dewaxing, Wax Deoiling

Solvent dewaxing removes wax (normal paraffins) from deasphalted lube base stocks. The main process steps include mixing the feedstock with the solvent, chilling the mixture to crystallize wax, and recovering the solvent. Commonly used solvents include toluene and methyl ethyl ketone (MEK). Methyl isobutyl ketone (MIBK) is used in a wax deoiling process to prepare food-grade wax.

3. CONVERSION

As mentioned in Section 1.1, the decreased use of kerosene lamps (thanks to Thomas Edison) coupled with rising demand for automotive gasoline provided incentives to convert kerosene and other heavier fractions into gasoline.

Table 10 illustrates the fundamental principle behind conversion. For a given class of hydrocarbons, “lighter” means lower molecular weight, lower boiling point, lower density, and higher hydrogen-to-carbon ratios (H/C). Methane, the lightest hydrocarbon, has an H/C of 4.0. Benzopyrene has an H/C of 0.6. The H/C of commonly used crude oils ranges from 1.5 to 2.0, and the H/C for asphaltenes is 1.15.

Table 10. Molecular Weight, H/C and Boiling Point for Selected Hydrocarbons

Compound	Molecular Weight	Formula	H/C	Boiling Point	
				°C	°F
Paraffins					
Methane	16.04	CH ₄	4.0	-164	-263.2
Ethane	30.07	C ₂ H ₆	3.0	-88.6	-127.5
Propane	44.10	C ₃ H ₈	2.67	-42.1	-43.7
Butane (iso)	58.12	C ₄ H ₁₀	2.50	-6.9	19.6
Octane (iso)	114.23	C ₈ H ₁₈	2.25	99.2	210.6
Cetane (normal)	226.44	C ₁₆ H ₃₄	2.13	287	548.6
Aromatics					
Benzene	78.11	C ₆ H ₆	1.0	80.1	176.2
Naphthalene	128.17	C ₁₀ H ₈	0.8	218	424.4
Benzopyrene	252.32	C ₂₀ H ₁₂	0.6	—	—

Most conversion processes – FCC, thermal cracking, and deasphalting – increase the H/C by rejecting carbon. A few processes – hydrotreating to a small extent and hydrocracking to a great extent – increase the H/C by adding hydrogen. In this context, “rejecting carbon” does not mean that a little bit of

carbon is removed from every molecule. Rather, it means that heavy molecules are split (“cracked”) into a smaller molecule with a higher H/C and another smaller molecule with a lower H/C. Molecules with low H/C – polyaromatic hydrocarbons (PAH) – can condense to form coke (*Figure 12*). Condensation reactions release hydrogen, lowering H/C even more.

3.1 Visbreaking

Visbreaking is a mild form of thermal cracking that achieves about 15% conversion of atmospheric residue to gas oils and naphtha. At the same time, a low-viscosity residual fuel is produced.

Visbreaking comes in two basic flavors – “short-contact” and “soaker.” In short-contact visbreaking, the feed is heated to about 900°F (480°C) and sent to a “soaking zone” (reactor) at 140 to 300 psig (1067 to 2170 kPa). The elevated pressure allows cracking to occur while restricting coke formation. To avoid over-cracking, the residence time in the soaking zone is short – several minutes compared to several hours in a delayed coker – and the hot oil is quenched with cold gas oil to inhibit further cracking and sent to a vacuum tower for product separation. “Soaker” visbreaking keeps the hot oil at elevated temperature for a longer time to increase the yield of middle distillates. The low-viscosity visbreaker gas oil can be sent to an FCC unit or hydrocracker for further processing, or used as heavy fuel oil.

3.2 Coking

Coking processes come in two basic forms – delayed coking, which is a semi-batch process, and fluid-bed coking, which is continuous.

3.2.1 Delayed Coking

In a delayed coker, vacuum residue feed is heated to about 900 to 970°F (487 to 520°C) and sent to a large coke drum. Cracking begins immediately, generating coke and cracked, vaporized products. Coke stays behind in the drum while the vapors rise to the top and flow to the product fractionator.

Liquid products include coker naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO). All of these require further processing due to their high olefins content, which makes them unstable and poorly suited for direct blending into finished products. The coker naphtha and LCGO are hydrotreated. The HCGO can go either to an FCC unit or a hydrocracker.

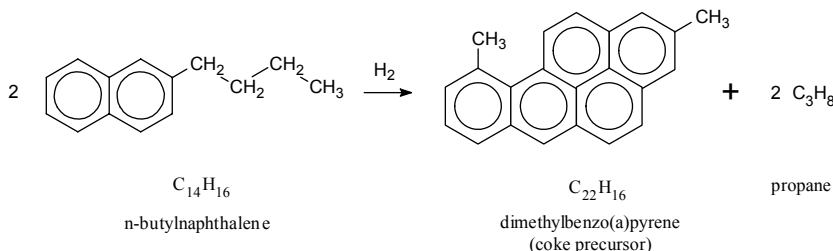


Figure 12. Representative thermal-cracking reaction. The reaction shown here is the sum of a condensation reaction, which generates hydrogen, and dealkylation, which consumes hydrogen.

Meanwhile, hot residue keeps flowing into the drum until it is filled with solid coke. To remove the coke, the top and bottom heads of the drum are removed. A rotating cutting tool uses high-pressure jets of water to drill a hole through the center of the coke from top to bottom. In addition to cutting the hole, the water also cools the coke, forming steam as it does so. The cutter is then raised, step by step, cutting the coke into lumps, which fall out the bottom of the drum. Typically, coke drums operate on 18- to 24-hour cycles, which include preheating the drum, filling it with hot oil, allowing coke and liquid products to form, cooling the drum, and decoking.

Coke can account for up to 30 wt% of the product. It can be shipped by rail, truck, or conveyor belt to a calciner, which converts **green coke** fresh from the drum into various grades of petroleum coke. Green coke can also be used for fuel.

Sponge Coke. Sponge coke is named for its sponge-like appearance. It is produced from feeds that have low-to-moderate asphaltene concentrations. If sponge coke meets certain specifications, it can be used to make carbon anodes for the aluminum industry. Otherwise, it is used for fuel. “Green” sponge coke must be calcined before it can be used for anodes. Fuel coke may not require calcination.

Needle Coke. Needle coke, named for its needle-like structure, is made from feeds that contain nil asphaltenes, such as hydrotreated FCC decant oils. Needle coke is a high-value product used to make graphite electrodes for electric-arc furnaces in the steel industry. At present (April 2004), needle coke fetches more than US\$500 per ton, which is significantly greater than the US\$40 to US\$45 per ton price for metallurgical coke exported from the United States.

Shot Coke. Shot coke is an undesirable product because it is inconsistent and in some cases dangerous. It is produced when the concentration of feedstock asphaltenes and/or coke-drum temperatures are too high. Excessive feedstock oxygen content can also induce its formation.

Shot coke begins to form as the oil flows into the coke drum. As light ends flash away, small globules of heavy tar are left behind. These globs of tar

coke rapidly grow due to the heat produced by asphaltene polymerization, producing discrete mini-balls 0.1 to 0.2 inches (2 to 5 mm) in diameter. In the center of the drum, the mini-balls can stick together to form clusters as large as 10 inches (25 cm). On occasion, a cluster breaks apart when the coke drum is opened, spraying a volley of hot mini-balls in every direction. Adding aromatic feeds, such as FCC decant oil, can eliminate shot coke formation. Other methods of eliminating shot coke – decreasing temperature, increasing drum pressure, increasing the amount of product recycle – decrease liquid yields, which is not desired.

A quantitative measure of the quality of coke is the coefficient of thermal expansion (CTE). A low CTE means that the product has a low tendency to expand when heated. Ranges of CTE for the three major types of petroleum coke are shown in *Table 11*.

Table 11. Coefficients of Thermal Expansion for Petroleum Coke Products

Product	CTE (cm/cm/°C x 10 ⁻⁷)
Needle coke	0 to 4
Sponge coke	8 to 18
Shot coke	>20

Shot coke cannot be used in making anodes for aluminum production, because the outer layer of a shot sphere has a very low CTE while the inside has a very high CTE. When rapidly heated, the interior expands, cracking the outer layer like an egg shell. Consequently, in aluminum smelters, shot-coke anodes quickly turn to dust.

Other specialty carbon products made from petroleum include recarburizer coke, which is used to make specialty steel, and titanium dioxide coke, which is used as a reducing agent in the titanium dioxide pigment industry.²⁹

3.2.2 Fluid Coking

Fluid coking, also called continuous coking, is a moving-bed process for which the operating temperature is higher than the temperatures used for delayed coking. In continuous coking, hot recycled coke particles are combined with liquid feed in a radial mixer (reactor) at about 50 psig (446 kPa). Vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The coke goes to a surge drum, then to a classifier, where the larger particles are removed as product. The smaller coke particles are recycled to a preheater, where they mix with fresh feed. Coking occurs both in the reactor and in the surge drum.

Installation costs for fluid coking are somewhat higher than for delayed coking, but feeds can be heavier and heat losses are lower.

3.3 Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) produces more than half the world's gasoline. A typical FCC unit comprises three major sections – riser/reactor, regenerator, and fractionation. *Table 12* provides important details on FCC.

Table 12. FCC in a Nutshell

Purpose	Convert heavy oils into gasoline and/or light olefins	
Licensors	Axens (IFP)	ExxonMobil
	KBR	Stone & Webster
	UOP	
Catalysts and Additives		
	Zeolite (highly acidic, catalyzes cracking)	
	Rare-earth oxide (increases catalyst stability)	
	ZSM-5 (increases octane and production of light olefins)	
	Pt (promotes combustion of CO to CO ₂ in regenerator)	
	Desox (transfers SO _x from regenerator to riser/reactor)	
Feeds	Atmospheric gas oil	Vacuum gas oil
	Coker gas oil	Deasphalted oil
	Lube extracts	Vacuum resid (up to 20 vol%)
Typical Feed Properties		
	Nitrogen	<3000 wppm
	Carbon residue	<5.0 wt%
	Nickel + Vanadium	<50 wppm
	90% boiling point	<1300°F (704°C)
Typical Process Conditions		
	Feed temperature	300 – 700°F (150 – 370°C)
	Reactor temperature	920 – 1020°F (493 – 550°C)
	Regenerator temperature	1200 – 1350°F (650 – 732°C)
	Catalyst/Oil ratio	4.0 – 10.0
	Reactor pressure	10 – 35 psig (170 – 343 kPa)
Typical Product Yields		
	Conversion	70 – 84 vol%
	H ₂ , H ₂ S, methane, ethane	3.0 – 3.5 wt%
	Propane and propylene	4.5 – 6.5 wt%
	Butanes and butenes	9.0 – 12.0 wt%
	Gasoline	44 – 56 wt%
	LCO	13 – 20 wt%
	Slurry oil	4 – 12 wt%
	Coke	5 – 6 wt%
	Total C ₃ -plus	106 – 112 vol%

3.3.1 FCC Process Flow

Figure 13 shows a sketch for the riser/reactor section of an FCC unit. In the reaction section, preheated oil is mixed with hot, regenerated catalyst. The mixture acts as a fluid because the catalyst particles are small – about the size of sifted flour. The hot catalyst vaporizes the oil, and the vaporized oil carries the catalyst up the riser/reactor. A book by Magee and Dolbear³⁰ provides

specific information on the manufacture and use of catalysts used for FCC and other refining processes.

The cracking reaction is very fast. It produces light gases, high-octane gasoline, and heavier products called light cycle oil (LCO), heavy cycle oil (HCO), slurry oil, and decant oil. It also leaves a layer of coke on the catalyst particles, making them inactive.

At the top of the riser, the temperature can reach 900 to 1020°F (482 to 549°C). The temperature at the riser outlet is a key factor in determining conversion and product selectivity, so FCC operators control it as tightly as possible. Higher temperatures favor production of olefin-rich light gas at the expense of gasoline, moderate temperatures favor gasoline production, and at lower temperatures gasoline yields decrease in favor of middle distillates.

In the disengaging section, steam is used to help separate the now-deactivated catalyst from the reaction products. The catalyst goes to the regenerator, where the coke is burned away by fluidized combustion in the presence of air. The hot catalyst at temperatures up to 1350°F (732°C) returns to the riser/reactor, where the cycle begins again.

In a 60,000 barrels-per-day unit processing a typical mixture of vacuum gas oils, the total catalyst in the unit (the “inventory”) is 400 to 500 tons. To maintain activity, about 0.5 to 1 wt% of the inventory is replaced each day. If the feed to the unit contains significant amounts of residue, the replacement rate is higher. The discharged catalyst is cooled and shipped either to a land fill for disposal or to another refiner, which may have a particular use for “conditioned” FCC catalyst.

3.3.2 Heat Balance

FCC units must be heat-balanced, or they won’t run. Understanding heat balance is the key to understanding how FCC variables interact. The burning of coke in the regenerator provides all of the heat required by the process. *Table 13* gives a representative breakdown of FCC heat requirements.

Table 13. Breakdown of FCC Heat Requirements

Heat-Consuming Event	Percent of Total
Heat up and vaporize fresh feed	40-50%
Heat recycled oil	0-10%
Heat of reaction (endothermic)	15-30%
Heat steam	2-8%
Heat losses	2-5%
Heat air to regenerator temperature	15-25%
Heat coke from the reactor to regenerator temperature	1-2%
Total Heat Duty	500-1000 Btu/lb 1160-2325 kJ/kg

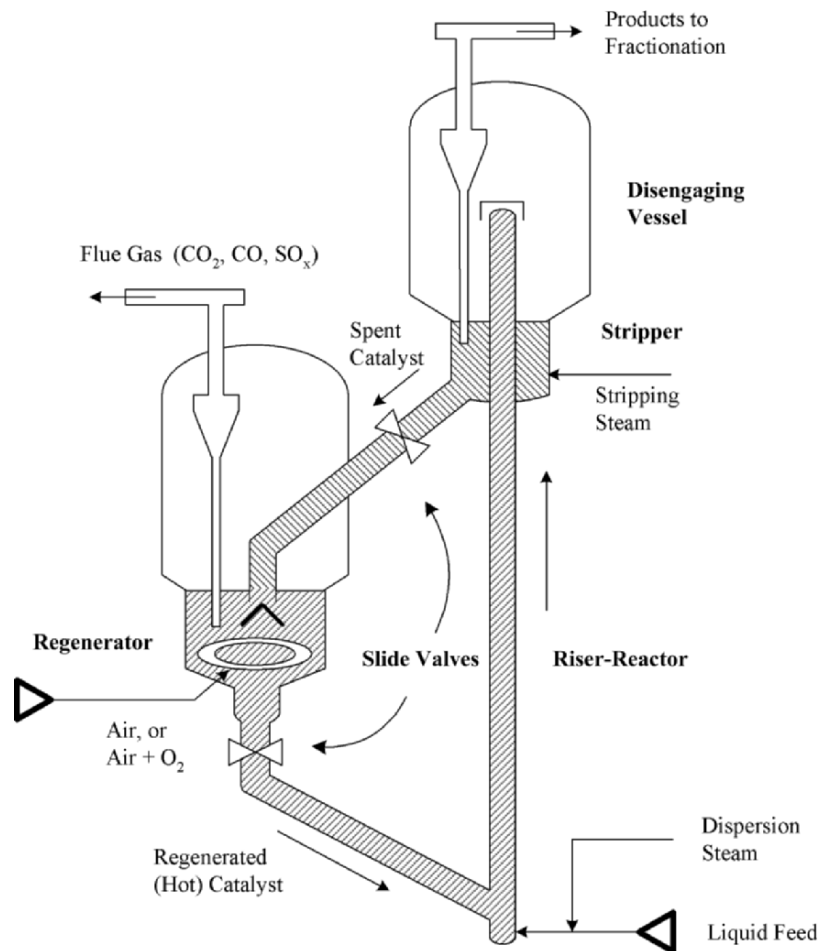


Figure 13. FCC riser-reactor and regenerator sections

3.3.3 Houdry Catalytic Cracking (HCC)

The Houdry Catalytic Cracking (HCC) process was a precursor to FCC. Houdry catalyst particles are pellets, which are carried to a storage hopper by a conveyor belt or pneumatic lift tubes. The pellets flow down from the hopper through the reactor, and from the reactor to a regenerator. The HCC product slate is similar to that for FCC, but FCC conversions and gasoline yields are significantly higher.

3.3.4 Residue FCC

Many modern FCC units are designed to process significant amounts of vacuum residue. These units use catalyst coolers (e.g., steam coils) in the regenerator or a second regeneration zone to remove excess heat from the unit. This is because vacuum residue generates substantially more coke than conventional FCC feeds, and excess heat is generated when the extra coke is burned away from catalyst.

In vacuum residue, the metals content can be very high – sometimes more than 200 wppm nickel-plus-vanadium. In an FCC unit, these metals are bad news. Nickel increases coke formation and decreases liquid yields. Vanadium reduces conversion, decreases liquid yields, and destroys the catalyst. For these reasons, refiners pretreat the residue in a hydrotreater before sending it on to the FCC.

In addition to removing most of the Ni and V, the pretreater decreases the concentration of sulfur, nitrogen, and aromatics. In the FCC, part of the feed sulfur ends up in liquid products and part ends up as sulfur oxides (SO_x) in the flue gas, so removing sulfur from the feed is beneficial. Removing nitrogen is beneficial because feed nitrogen suppresses FCC catalyst activity. Saturating feed aromatics increases FCC conversion by as much as 10 vol%. This alone can justify the cost of building the pretreater.

3.4 Hydrotreating and Hydrocracking

A modern petroleum refinery may have four or more hydrotreating units. Strictly speaking, hydrotreaters are not conversion units because the breaking of carbon-to-carbon bonds is minimal. However, it is convenient to discuss hydrotreating together with hydrocracking and mild hydrocracking because they employ similar catalysts and process flow schemes.

The key differences are presented in Table 14. Hydrocrackers tend to operate at higher pressure, using different catalysts, and with lower linear hourly space velocity (LHSV). LHSV is equal to the volume of feed per hour divided by the catalyst volume. A lower required LHSV means that a given volume of feed requires more catalyst. In terms of process conditions and conversion, mild hydrocracking lies somewhere between hydrotreating and full-conversion hydrocracking.

Table 14. Comparison of Hydrotreating, Hydrocracking and Mild Hydrocracking

Table 17: Comparison of Hydrotreating, Hydrocracking and Mild Hydrocracking			
Process, Feedstock Types	H ₂ Partial Pressure		Conversion
	psig	kPa	
<i>Hydrotreating</i>			
Naphtha	250 – 300	1825 – 2170	0 – 5%
LGO (Kerosene)	250 – 600	1825 – 4238	0 – 5%
HGO (Diesel), LCO	600 – 800	4238 – 5617	5 -15%
VGO, VBGO, CGO, HCO	800 – 2000	5617 – 13,890	5 -15%
Residual Oil	2000 – 3000	13,890 – 20,786	5 -15%
<i>Mild Hydrocracking</i>			
VGO, VBGO, CGO, LCO, HCO	800 – 1500	5617 – 10,443	20 – 40%
<i>Hydrocracking</i>			
VGO, VBGO, CGO, LCO, HCO	1500 – 2000	10,443 – 13,890	60 – 99%
Residual Oil	2000 – 3000	13,890 – 20,786	15 – 25%
LGO = Light Gas Oil			
HGO = heavy Gas Oil			
LCO = FCC Light Cycle Oil			
HCO = FCC Heavy Cycle Oil			
VGO = Vacuum Gas Oil			
VBGO = Visbreaker Gas Oil			
CGO = Coker Gas Oil			

3.4.1 Chemistry of Hydrotreating and Hydrocracking

To one extent or another, all of the chemical reactions listed in Table 15 occur in hydrotreaters and hydrocrackers. The reactions are discussed in greater detail in Chapters 7-9.

Table 15. List of Hydrotreating and Hydrocracking Reactions

Hydrotreating (C-C bond breaking is minimal)	Hydrocracking (C-C bond breaking is significant)
Hydrosulfurization (HDS)	Dealkylation of aromatic rings
Hydrodenitrogenation (HDN)	Opening of naphthene rings
Hydrodemetallation (HDM)	Hydrocracking of paraffins
Saturation of aromatics	
Saturation of olefins	
Isomerization	

3.4.2 Hydrotreating Process Flow

Figure 14 illustrates the process flow for a fixed-bed hydrotreater. At moderate-to-high pressure – 300 to 1800 psig (2170 to 12,512 kPa) – mixtures of preheated oil and hydrogen pass down over fixed beds of catalyst, in which the desired reactions occur.

Hydrotreating is exothermic (heat-releasing), so many commercial units comprise several catalyst beds separated by quench zones. In a quench zone, hot process fluids from the preceding bed are mixed with relatively cold, hydrogen-rich quench gas before passing to the next bed.

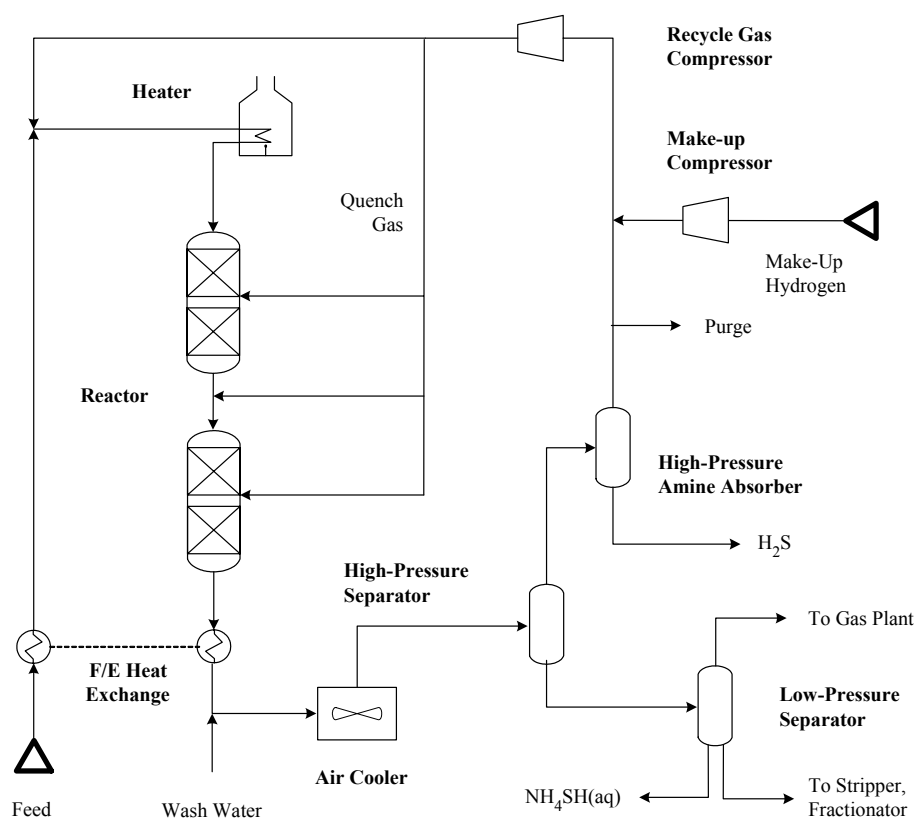


Figure 14. Gas-oil hydrotreating and once-through hydrocracking

HDS and HDN reactions produce H_2S and NH_3 , respectively. Wash water is injected into the effluent from the last reactor to remove ammonia, which goes into the aqueous phase as ammonium bisulfide, $NH_4HS(aq)$. The $NH_4HS(aq)$ is rejected from the unit as sour water in downstream flash drums.

In the high-pressure flash drum, liquid products are separated from the hydrogen-rich gas, which is recycled to the reactors. In most hydrotreaters designed for deep desulfurization, H_2S is removed from the recycle gas with a high-pressure amine absorber. The liquids go to a stripping column, which removes entrained H_2S and other light gases. These go to a low-pressure amine absorber and then to either a gas plant or the refinery fuel-gas system.

The destination of the liquid is unit-specific. In some hydrotreaters, the stripped liquid goes directly to product blending. In others, it goes to one or more fractionation towers.

Naphtha Hydrotreating. Heavy naphthas generally have low octane numbers, often less than 60 RON. To raise the octane, refiners use catalytic reforming units. Alternatively, heavy naphtha can go to an isomerization unit, which also makes high-octane products. In both reforming and isomerization, the catalysts are sulfur-sensitive, so a naphtha hydrotreater is used to lower the feed sulfur content, usually to <1 wppm. Some nitrogen is removed, too, which also is beneficial.

Table 16 provides additional details on hydrotreating.

Table 16. Hydrotreating in a Nutshell

Purpose	Sulfur removal (HDS) Olefin saturation Metals removal	Nitrogen removal (HDN) Aromatic saturation (HDA)
Licensors	Axens (IFP) Chevron Lummus (CLG) Haldor-Topsoe Shell Global Solutions	CDTECH ExxonMobil KBR UOP
Catalysts	CoMo on γ -alumina for HDS NiMo or NiW on γ -alumina for HDS, HDN, aromatic saturation	
Feeds	Naphtha Heavy gas oil Coker gas oil	Kerosene Vacuum gas oil Residual oils
Typical Process Conditions		
	Reactor temperature	600 – 800°F (315 – 425°C)
	Reactor pressure	250 – 2000 psig (1825 – 13,890 kPa)

3.4.3 Hydrotreating Objectives

Catalytic hydrotreating removes contaminants from liquid petroleum fractions. It also saturates most olefins and many aromatic compounds. Sulfur, nitrogen, oxygen, and metals are the most troublesome impurities. If not removed, they can deactivate catalysts, contaminate finished products, and accelerate corrosion in downstream equipment.

Gasoline Hydrotreating. In the context of post-treating gasoline to meet recent sulfur specifications, Section 8.2.5 discusses gasoline hydrotreating. Temperatures and pressures are relatively mild, but the leading processes use multiple catalysts, multiple catalyst beds, and/or pre-fractionation to minimize loss of gasoline octane.

Kerosene Hydrotreating. Straight-run kerosene streams may not meet specifications for jet-fuel. By using mild hydrodearomatization (HDA) to convert some aromatic compounds into cleaner-burning naphthenes, low-severity hydrotreating can convert kerosene into jet fuel. In many parts of the world, low-sulfur kerosene is used for home heating. In those regions, straight-run kerosene and other light gas oils usually must be hydrotreated.

Diesel Hydrotreating. From 1991 in Sweden, 1995 in California, and 1998 in the rest of the U.S., hydrotreating was used to make diesel containing <500 wppm sulfur. Generally, diesel hydrotreaters operate at higher pressures than naphtha and kerosene units, and they often use different catalysts. These days, under pressure to make ULSD by the end of 2006, most U.S. refiners either have or will be (a) building new diesel hydrotreaters, (b) revamping existing units by changing catalysts, modifying reactor internals, adding a high-pressure H₂S absorber, and/or adding a new reactor, or (c) converting other units to diesel service.

FCC Feed Pretreating: VGO, CGO, and VBGO. For hydrotreaters that prepare feed for conventional FCC units, removing nitrogen (HDN) from the feed is beneficial, because organic nitrogen (especially basic nitrogen) inhibits cracking by binding to the highly acidic active sites in FCC catalysts. The removal of sulfur (HDS) can reduce the size of, or eliminate the need for, FCC gasoline post-treating units. By converting aromatics to naphthenes (HDA), FCC feed pretreaters increase feed “crackability.” In FCC and other thermal cracking units, naphthenes convert to lighter products. But except for losing side chains, aromatics are rather inert. If anything, they tend to form polyaromatic hydrocarbons (PAH) and coke. Pretreaters also benefit FCC units by removing metals (primarily nickel and vanadium) and Conradson carbon (CCR). CCR correlates strongly with the tendency of a feed to form coke in a delayed coking unit. It also correlates with coke-formation in an FCC unit. By reducing feed CCR, a pretreater allows an FCC to operate at higher feed rates and/or higher conversion. If the feed rate stays constant, the conversion can increase by 10 to 20 vol%. The extent of the increase depends upon the properties of the raw feed and the conditions under which the feed is hydrotreated.

FCC Feed Pretreating: Residue. Originally, residue hydrotreaters were built to reduce the sulfur content of heavy fuel oil. These days, a large percentage of residue hydrotreaters are used to pretreat FCC feeds. Residue hydrotreating requires higher pressure, lower LHSV, and at least one hot flash drum after the reactors. Another main difference is the need to use one or more HDM catalysts to protect the HDS catalyst from metals such as nickel and vanadium. If not removed, Ni and V accelerate deactivation and the buildup of pressure-drop. In the Resid Unionfining process offered by UOP, HDM catalyst is loaded into a guard reactor upstream from the main reactors. In the RDS process offered by Chevron Lummus Global, an OCR (“onstream catalyst replacement”) or UFR (“up-flow reactor”) unit removes metals from the RDS feed. With OCR, a refiner can process residues containing 400 wppm metals (Ni + V).

Lube Hydrotreating. The mild hydrotreating (“hydrofinishing”) of lube oils improves color, odor, and stability by removing olefins, sulfides and mercaptans. Severe hydrotreating also removes aromatics, nitrogen, and refractory sulfur compounds.

Pyrolysis Gasoline Hydrotreating. Hydrotreating improves the quality of pyrolysis gasoline (pygas), a by-product from olefins plants. In the past, due to its high octane, some pygas was blended into gasoline. Pygas contains diolefins, which react with air to form gums. Mild hydrotreating converts diolefins into mono-olefins. This improves the stability of pygas.

3.4.4 Hydrocracking

As shown in Table 14, the major difference between hydrotreating, hydrocracking, and mild hydrocracking is the extent to which conversion occurs. In a hydrocracking unit designed for high conversion of vacuum gas oil, the process flow is more complex. The unit probably operates at a much higher pressure. It may include an additional reactor, a hot high-pressure separator, and a multiple-column fractionation section. To achieve near-total conversion of fresh feed, unconverted oil may be recycled. Some details about hydrocracking are given in Table 17.

3.4.5 Hydrocracking Objectives

For a given hydrocracker, process objectives can include:

- Maximum production of naphtha
- Maximum production of middle distillate fuels
- Flexibility to swing between production of naphtha and middle distillates
- Production of ultra-clean lube base stocks
- Production of olefin plant feeds.

3.4.6 Hydrocracker Feeds

Liquid feeds can be atmospheric or vacuum gas oils from crude distillation units; gas oils (light and heavy) from delayed cokers, fluid cokers, or visbreakers; and cycle oils (light and heavy) from FCC units.

3.4.7 Hydrocracking Process Flow

The process flow scheme in Figure 14 can describe a gas-oil hydrotreater, a mild hydrocracking, or a once-through high-conversion hydrocracker. In a hydrocracker, the first few beds are likely to contain hydrotreating catalyst while subsequent beds contain hydrocracking catalyst. In some hydrocrackers designed for maximum production of diesel fuel, all catalyst beds contain hydrocracking catalyst. Other hydrocracking process flow schemes are described in Chapters 7 and 8.

3.4.8 Hydrocracker Products

Middle distillates (jet and diesel) from high-conversion hydrocrackers meet or exceed finished product specifications. The heavy naphtha, however, usually goes to a catalytic reformer for octane improvement. The fractionator bottoms from partial conversion units can be sent to an FCC unit, an olefins plant, or a lube plant.

Due to the fact that products from a hydrocracker are less dense than the feeds, the total volume of liquid products is greater than the feed volume by 10 to 30 vol%. This phenomenon is called volume swell.

Table 17. Hydrocracking in a Nutshell

Purpose	Convert heavy hydrocarbons into lighter hydrocarbons	
Uses for Unconverted Oil		
	FCC feed	Lube base stock
	Olefin plant feed	Recycle to extinction
Other Reactions		
	Sulfur removal (HDS)	Nitrogen removal (HDN)
	Olefin saturation	Aromatic saturation
Licensors		
	Axens (IFP) (IFP)	Chevron Lummus
	ExxonMobil	KBR
	Shell Global Solutions	UOP
Catalysts		
	NiMo on γ -alumina (HDS, HDN, aromatic saturation)	
	NiMo or NiW on zeolite (hydrocracking)	
	NiMo or NiW on amorphous silica-alumina (hydrocracking)	
	Pd on zeolite (hydrocracking)	
Feeds		
	Heavy gas oil	Vacuum gas oil
	Coker gas oil	Residual oils
Typical Process Conditions		
	Reactor temperature	600 – 800°F (315 – 425°C)
	Reactor pressure	1200 – 2500 psig (8375 – 17,338 kPa)
Range of Product Yields		
	Conversion (once-through)	20 – 90 vol%
	Conversion (with recycle)	90 – 99 vol% fresh feed
	C ₄ -plus naphtha	Up to 120 vol% fresh feed
	Middle distillates	Up to 90 vol% fresh feed
	Hydrogen consumption	1000 to 3000 scf/bbl
		175 to 525 Nm ³ /m ³

3.5 Ebullated Bed Units

In fixed-bed hydrocrackers designed to process VGO, residual oils in the feed can reduce catalyst cycle life if they contain even trace amounts of salts, asphaltenes, refractory carbon, trace metals (Fe, Ni, V), or particulate matter. As mentioned in Section 3.4.2, fixed-bed units designed to process residue remove metals and other contaminants with upstream guard beds or onstream catalyst replacement technology. In contrast, ebullated bed hydrocrackers can and do process significant amounts of residual oils. This is because fresh

catalyst is added and spent catalyst is removed continuously. Consequently, catalyst life does not impose limitations on feed selection or conversion.

Ebullated bed processes are offered for license by Axens (IFP) ABB Lummus. In ebullated bed reactors, hydrogen-rich recycle gas bubbles up through a mixture of oil and catalyst particles to provide three-phase turbulent mixing. The reaction environment can be nearly isothermal, which improves product selectivity. At the top of the reactor, catalyst particles are disengaged from the process fluids, which are separated in downstream flash drums. Most of the catalyst goes back to the reactor. Some is withdrawn and replaced with fresh catalyst.

4. UPGRADING NAPHTHA

Gasoline is produced by blending several different refinery streams – butanes, straight-run gasoline, reformate, alkylate, isomate, FCC gasoline, oxygenates, and others. This section gives an overview of the processes that either upgrade or generate gasoline blend stocks.

4.1 Catalytic Reforming

4.1.1 Catalytic Reforming Objectives

Catalytic reforming converts low-octane heavy naphtha into a high-octane product (reformate) that is an excellent gasoline blend stock. Reformate has a high content of BTX (benzene-toluene-xylene), so it also serves as a great source of aromatics for petrochemical plants.

In addition to making aromatic compounds, catalytic reformers produce hydrogen, which is used in hydrotreaters, hydrocrackers, and other hydrogen-addition processes.

4.1.2 Chemistry of Catalytic Reforming

The chemistry of catalytic reforming includes the reactions listed in *Table 18*. All are desirable except hydrocracking, which converts valuable C₅-plus molecules into light gases. The conversion of naphthenes to aromatics and the isomerization of normal paraffins provide a huge boost in octane. H₂ is produced by dehydrocyclization of paraffins and naphthene dehydrogenation, which are shown in *Figure 15*.

Table 18. List of Catalytic Reforming Reactions

Naphthene Reactions	Paraffin Reactions
Dehydrogenation to form aromatics	Dehydrocyclization to form aromatics
Isomerization to form different naphthenes	Isomerization to form other paraffins
	Hydrocracking to form C ₄ -minus

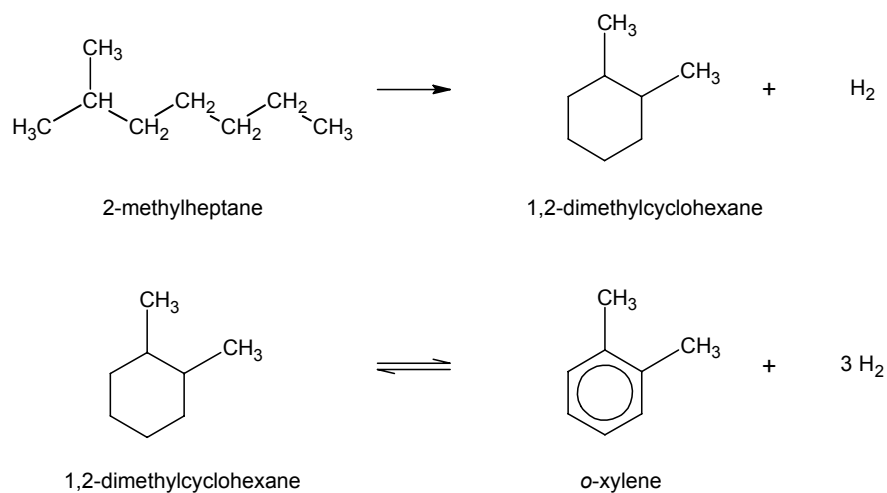


Figure 15. Dehydrocyclization and dehydrogenation

Hydrocracking and isomerization reactions are shown in *Figure 16* and *Figure 17*, respectively. Hydrocracking, which is undesirable in this process, occurs to a greater extent at high temperatures.

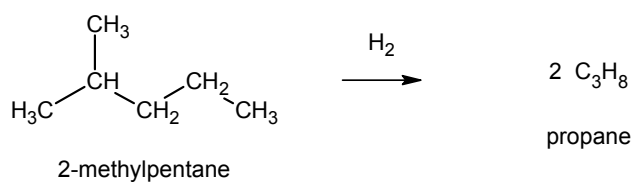


Figure 16. Hydrocracking in catalytic reformers.

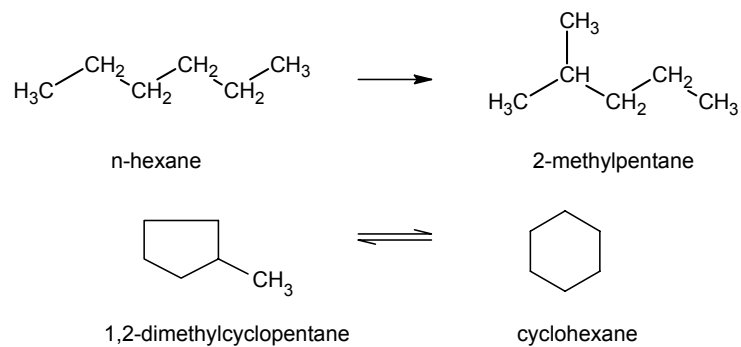


Figure 17. Isomerization of paraffins and naphthenes in catalytic reformers.

Additional details about catalytic reforming are given in *Table 19*.

Table 19. Catalytic Reforming in a Nutshell

Purpose	Increase heavy-naphtha octane	
Other	Produce aromatics (BTX) for petrochemical plants Produce hydrogen	
Licensors	Axens (IFP) ExxonMobil	BP UOP
Catalysts	Pt on γ -alumina Pt-Re-Sn on γ -alumina	Pt-Re on γ -alumina
Promoters	HCl	
Feeds	Hydrotreated heavy naphtha, 40 to 62 RON	
Typical Process Conditions		
	H ₂ /HC ratio	Up to 6.0
	Reactor inlet temperature	900 – 970°F (482 – 521°C)
	Pressure (Semi-regen., Cyclic)	200 – 500 psig (1480 – 3549 kPa)
	Pressure (CCR)	100 – 150 psig (791 – 1136 kPa)
Typical Product Yields and Properties		
	Total C ₅ -plus	84 to 85 vol%
	H ₂ production	650 – 1100 scf/bbl (115 – 195 Nm ³ /m ³)
	RONC (Semi-regen., Cyclic)	85 to 95
	RONC (CCR)	Up to 105

4.1.3 Catalytic Reforming Catalysts

Catalytic reforming catalysts contain highly dispersed platinum (Pt), the activity of which is inhibited by sulfur. Therefore, an upstream hydrotreater lowers the sulfur content of reformer feeds to <1 wppm. In addition to Pt, modern multi-metallic catalysts contain highly dispersed rhenium (Re) and in some cases tin (Sn).

4.1.4 Process Flows

There are three major process flows for catalytic reforming:

- Semi-regenerative
- Cyclic
- Continuous catalyst regeneration (CCR)

Figure 18 shows a semi-regenerative reformer, a fixed-bed unit in which catalyst cycles last from 6 to 12 months. A catalyst cycle ends when the unit is unable to meet its process objectives – typically octane and overall C₅-plus yields. At the end of a cycle, the entire unit is brought down and catalyst is regenerated. In a cyclic reformer, catalyst cycles are shorter – 20 to 40 hours – but they are staggered so that only one reactor goes down at a time. In a CCR unit, the catalyst is slowly but constantly moving from the reactor to the regenerator and back again.

In a semi-regenerative unit, desulfurized naphtha is mixed with hydrogen, heated to $>900^{\circ}\text{F}$ ($>480^{\circ}\text{C}$) and passed through a series of fixed-bed reactors. The major chemical reactions – dehydrogenation and dehydrocyclization – are endothermic (heat absorbing), and the reactors themselves are essentially adiabatic. This means that heat can't enter or leave except by the cooling or heating of reaction fluids. Consequently, the temperature drops as reactants flow through a reactor. Between reactors, fired heaters bring the process fluids back to desired reactor inlet temperatures.

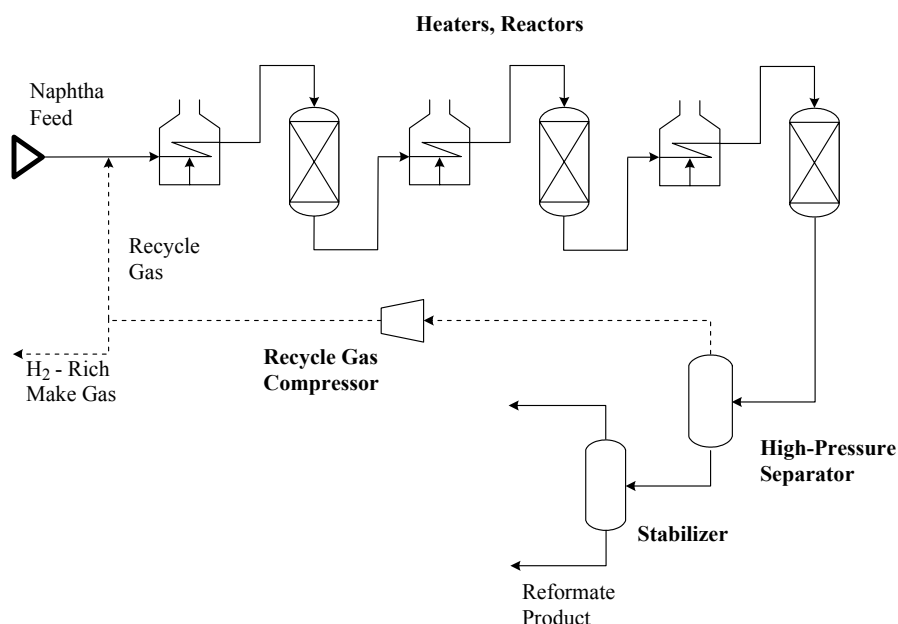


Figure 18. Semi-regenerative catalytic reforming

Some catalytic reformers operate at low pressure (100 psig, 791 kPa), while others operate at >500 psig (3549 kPa). Low operating pressure improves yields of aromatics and hydrogen, but it accelerates catalyst deactivation by increasing the rate at which coke forms on the catalyst. In a CCR reformer, the catalyst always is being regenerated, so increased coking is less problematic. Therefore, CCR units can operate at very low pressures. In most reformers, the feed is spiked with an organic chloride, which converts to hydrogen chloride (HCl) in the reactors. The HCl increases catalyst acidity and helps to minimize catalyst coking.

The effluent from the last reactor is cooled and sent to a separator, from which hydrogen-rich gas is removed and recycled to the reactors. The liquid product flows to a stabilizer column, where entrained gases are removed, before going to the gasoline blender or aromatics plant.

In a CCR unit (*Figure 19*), the hydrotreated feed mixes with recycle hydrogen and goes to series of adiabatic, radial-flow reactors arranged in a vertical stack. Catalyst flows down the stack, while the reaction fluids flow radially across the annular catalyst beds. The predominant reforming reactions are endothermic, so heaters are used between reactors to reheat the charge to reaction temperature. Flue gas from the fired heaters is typically used to generate steam.

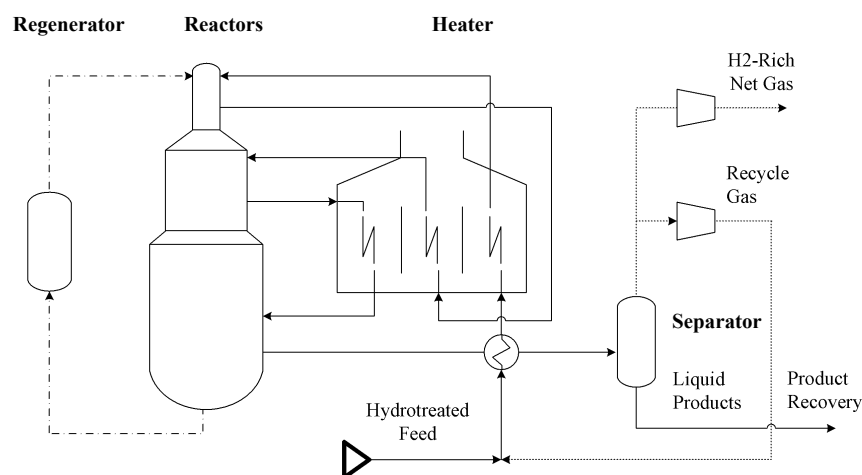


Figure 19. CCR catalytic reforming

The effluent from the last reactor is cooled and sent to a separator. Part of the vapor is compressed and recycled to the reactors. The rest is compressed, combined with separator liquids, and sent to the product recovery section. Liquids from the recovery section go to a stabilizer, where light saturates are removed from the C₆-plus aromatic products.

Partly deactivated catalyst is continually withdrawn from the bottom of the reactor stack and sent to the regenerator. As the catalyst flows down through the regenerator, the coke is burned away. Regenerated catalyst is lifted by hydrogen to the top of the reactor stack. Because the reactor and regenerator sections are separate, each operates at its own optimum conditions. The regeneration section can be temporarily shut down for maintenance without affecting the operation of the reactor and product recovery sections.

4.2 Isomerization

4.2.1 Isomerization Objectives

As we have seen, isomerization occurs as a side-reaction in all conversion processes. But in refining, when we say “isomerization process,” we are referring specifically to the on-purpose isomerization of n-butane, n-pentane, and n-hexane. The main purpose of n-paraffin isomerization is to produce iso-paraffins with substantially higher octane numbers. An isomerization reaction for normal hexane was shown in *Figure 17*.

Some details about paraffin isomerization processes are given in *Table 20*.

Table 20. Isomerization in a Nutshell

Purpose	Convert n-butane to isobutane Convert n-pentane and n-hexane to branched isomers	
Licensors (C₄)	ABB Lummus Global UOP	BP
Licensors(C₅C₆)	Axens (IFP) UOP	BP
Catalysts(C₄)	Pt on γ -alumina, HCl promoter	Pt on zeolite
Catalysts(C₅C₆)	Pt on γ -alumina, HCl promoter	Pt on zeolite
Feeds(C₄)	dry n-butane	
Feeds(C₅)	Light straight-run, end point <160°F (71°C)	
	Light reformat	Light hydrocrackate
	Natural gasoline	Light aromatics raffinate
Process Conditions (Pt on alumina, chlorided)		
	Reactor temperature	250 – 300°F (121 – 149°C)
	Reactor pressure	400 – 450 psig (2859 – 3204 kPa)
Process Conditions (Pt on zeolite)		
	Reactor temperature	445 – 545°F (230 – 285°C)
	Reactor pressure	190 – 440 psig (1411 – 3135 kPa)
Conversion and Product Properties (C₅C₆)		
	Conversion (with recycle)	up to 97%
	RON	85 to 90

Section 8.2.1 lists octane numbers for heavy naphtha and some normal and iso-paraffins. N-butane has a high octane number (92), so refiners blend as much of it as possible into gasoline. But n-butane also evaporates easily, which means that tighter restrictions on the RVP (volatility) of gasoline limit its C₄ content (see Section 8.2.2). In many locales, this creates an excess of n-butane. By converting it into isobutane, which is consumed in alkylation units, refiners can reduce or eliminate this excess of n-butane.

4.2.2 Isomerization Catalysts

The most common catalyst for isomerising n-butane is platinum (Pt) on alumina promoted by chloride. The high activity of this catalyst allows operation at relatively low temperature. This is beneficial because the reaction is controlled by equilibrium; at low temperature, equilibrium favors isobutane. Pt/alumina catalysts can't be regenerated, and they are highly sensitive to water and other contaminants.

In units that isomerize n-pentane and n-hexane, the reactions are catalyzed either by Pt/alumina or Pt on zeolite. The zeolite catalysts require higher temperatures, but they are less sensitive to water. As with butane isomerization, the reactions are controlled by equilibrium, so lower reaction temperatures favor branched isomers. The high temperatures required by zeolite catalysts reduce the octane of the product relative to products made at lower temperatures with chlorided alumina catalysts.

4.2.3 Process Flow: C₄ Isomerization

The feed to a butane (C₄) isomerization unit should contain maximum amounts of n-butane and only small amounts of isobutane, pentanes, and heavier material. The feed is dried, combined with dry makeup hydrogen, and charged to the reactor section at 230 to 340° F (110 to 170°C) and 200 to 300 psig (1480 to 2170 kPa). H₂ is not consumed by isomerization reactions, but it suppresses polymerization of the olefin intermediates that are formed during the reaction. A small amount of organic chloride promoter, which is added to maintain catalyst activity, converts completely to HCl in the reactors.

Often, two reactors in series are used to increase on-stream efficiency. The catalyst in one reactor can be replaced while the other continues to operate. The reactor effluent (isomerate) flows to a stabilizer. A caustic scrubber removes HCl from the separated light gases. The stabilized liquid product comprises a near-equilibrium mixture of n-butane and isobutanes, plus a small amount of heavier hydrocarbons. Losses due to cracking are less than 1 wt%.

The isomerate can be blended directly into gasoline or sent to an alkylation unit. N-butane from an alkylation unit can be recycled to a butane isomerization unit to achieve nearly total conversion of n-butane into isobutane or alkylate.

4.2.4 Process Flow: C₅C₆ Isomerization

Pentane/hexane (C₅C₆) isomerization processes increase the octane of light gasoline. In a typical unit, dried, hydrotreated feed is mixed with a small amount of organic chloride and recycled hydrogen, then heated to reaction temperature.

Process objectives determine whether one or two reactors are used. In two-reactor units (*Figure 20*), the feed flows first to a saturation reactor, which removes olefins and (to a large extent) benzene. After saturation, the feed goes to an isomerization reactor, where normal paraffins are converted to isoparaffins.

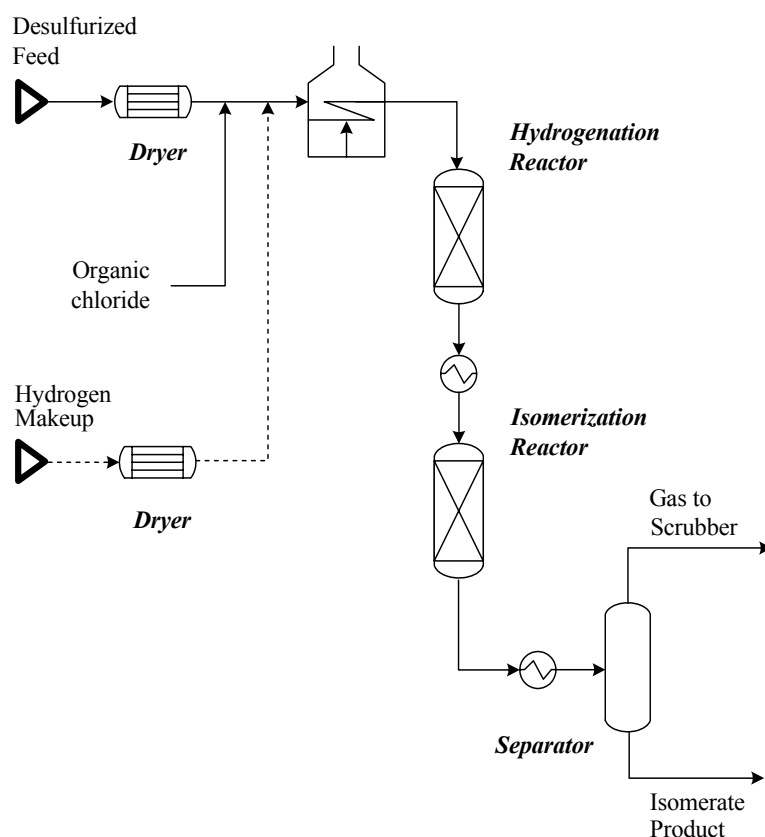


Figure 20. C_5C_6 isomerization: two reactors, once-through hydrogen

The reactor effluent flows to a product separator, where hydrogen is separated from the other reaction products. Recovered hydrogen can go to a recycle compressor, which returns it to the reactors, or it can be treated and sent to the fuel gas system. Separator liquids go to a stabilizer column, which removes light gases and remaining dissolved hydrogen. The stabilized liquid goes to storage or gasoline blending. If sent to a fractionator, n-pentane and n-hexane can be recycled to the isomerization unit for increased conversion.

4.3 Catalytic Oligomerization

4.3.1 Catalytic Oligomerization Objectives

Catalytic oligomerization also is called catalytic polymerization, catpoly, and catalytic condensation. The process converts C_3 and C_4 olefins into C_6 to C_9 olefins, which are excellent gasoline blend stocks. Per *Table 22*, the research octane numbers for C_6 and C_8 olefins such as methyl-2-pentenes and 2,2,4-trimethylpentenes are greater than 97.

Variations on the process make higher olefins and aromatics such as cumene for petrochemical applications. *Figure 21* shows the main chemical reaction for the dimerization of isobutylene.

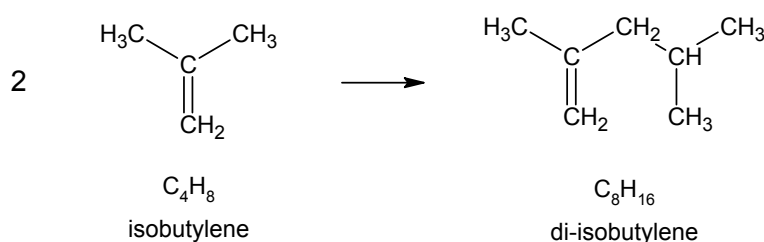


Figure 21. Dimerization of isobutylene

4.3.2 Catalysts

Sulfuric acid, phosphoric acid, and solid phosphoric acid on kieselguhr pellets (SPA) are used as catalysts. The SPA catalyst is non-corrosive, so it can be used in less-expensive carbon-steel reactors.

4.3.3 Process Flow

Figure 22 presents a sketch for a unit designed to use SPA catalysts. After pre-treatment to remove sulfur and other undesirable compounds, the olefin-rich feed is sent to the reactor. The reaction is exothermic, so temperatures are controlled by diluting the feed with product and by injecting relatively cold feedstock (quench) between beds in the reactor. Temperatures range from 300 to 450°F (150 to 230°F) and pressures range from 200 to 1,200 psig (1480 to 8375 kPa).

Reaction products go to stabilization and/or fractionator systems to separate gases – saturated and unsaturated C_3 - C_4 compounds – from the liquid product. The gases are recycled to the reactor, and the liquid product goes to gasoline blending.

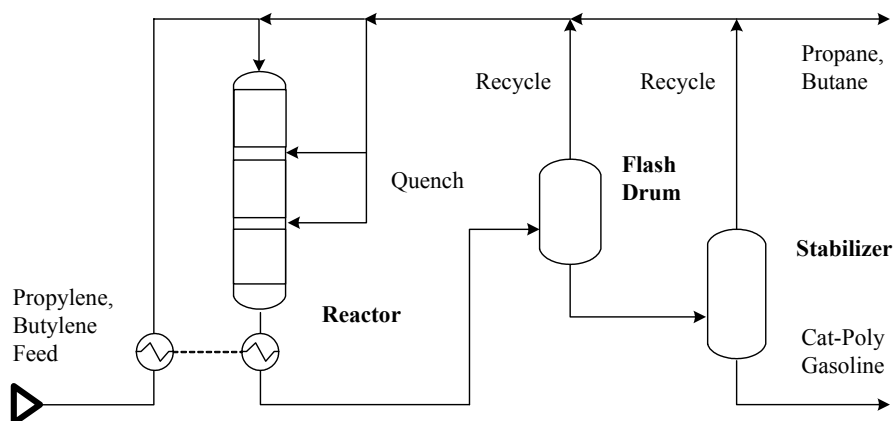


Figure 22. Catalytic oligomerization of olefins

4.4 Alkylation

4.4.1 Alkylation Objectives

Alkylation processes combine light olefins (primarily propylene and butylene) with isobutane in the presence of a highly acidic catalyst, either sulfuric acid or hydrofluoric acid. The product (alkylate) contains a mixture of high-octane, branched-chain paraffinic hydrocarbons. *Figure 23* illustrates the reaction between isobutane and trans-2-butene. Alkylate is a highly desirable gasoline blend stock because, in addition to its high octane, it has a low vapor pressure. The octane of the product depends on the operating condition and the kinds of olefins used.

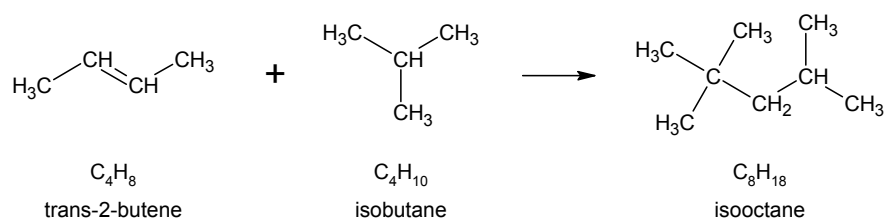


Figure 23. Alkylation of trans-2-butene

4.4.2 Process Flow: Sulfuric Acid Alkylation

In sulfuric acid (H_2SO_4) alkylation units, the feeds – propylene, butylene, amylene, and fresh isobutane – enter the reactor and contact sulfuric acid

with a concentration of 85 to 95%. The reactor is divided into zones. Olefins are fed through distributors to each zone, and sulfuric acid and isobutanes flow over baffles from one zone to the next.

The reactor effluent goes to a settler, in which hydrocarbons separate from the acid. The acid is returned to the reactor. The hydrocarbons are washed with caustic and sent to fractionation. The fractionation section comprises a depropanizer, a deisobutanizer, and a debutanizer. Alkylate from the deisobutanizer can go directly to motor-fuel blending, or it can be reprocessed to produce aviation-grade gasoline. Isobutane is recycled.

4.4.3 Process Flow: HF Alkylation

Figure 24 shows a process schematic for hydrofluoric acid (HF) alkylation. Olefins and isobutane are dried and fed to a reactor, where the alkylation reaction takes place over the HF catalyst. The reactor effluent flows to a settler, where the acid phase separates from the hydrocarbon phase. The acid is drawn off and recycled. The hydrocarbon phase goes to a deisobutanizer (DIB). The overhead stream, containing propane, isobutane, and residual HF, goes to a depropanizer (DeC3). The DeC3 overhead goes to an HF stripper. It is then treated with caustic and sent to storage. Isobutane from the DIB main fractionator is recycled. The bottom stream from the debutanizer goes to product blending.

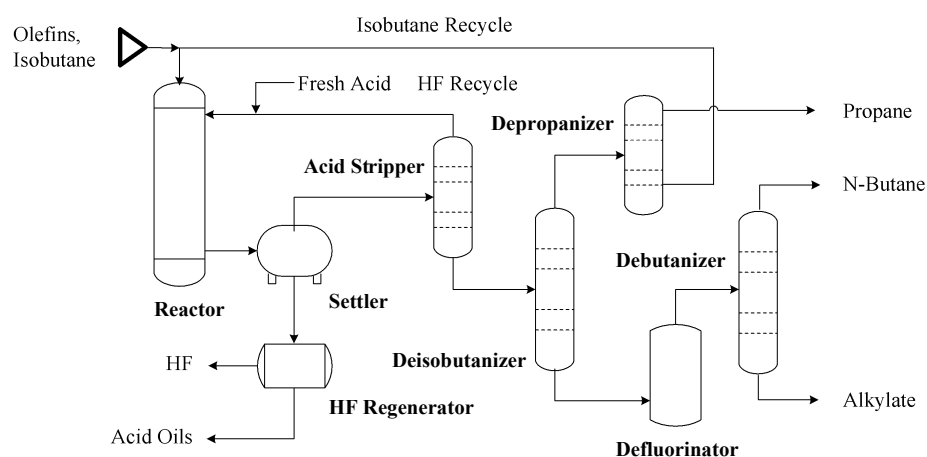


Figure 24. HF alkylation

5. LUBES, WAXES AND GREASES

“Bottom of the barrel” fractions – atmospheric and vacuum residues – can be converted by the processes described in Sections 2 and 3, or they can be used to make lubes, waxes and greases.

5.1 Lube Base Stocks

Refiners prepare lube base stocks from residual oils by removing asphaltenes, aromatics, and waxes. Lube base stocks are hydrofinished, blended with other distillate streams for viscosity adjustment, and compounded with additives to produce finished lubricants.

Solvent-based processes for removing asphaltenes, aromatics and waxes were discussed in Section 2.2. The next few paragraphs give a quick overview of catalytic dewaxing.

5.1.1 Catalytic dewaxing

Catalytic dewaxing (CDW) was developed by Exxon Mobil in the 1980s. The process employs a shape-selective zeolite called ZSM-5, which selectively converts waxy n-paraffins into lighter hydrocarbons.

The Isodewaxing Process, commercialized in 1993 by ChevronTexaco, catalytically isomerizes n-paraffins into iso-paraffins. This decreases the wax content and increases the concentration low-viscosity hydrocarbons, both of which are desirable. Isodewaxing also removes sulfur and nitrogen, and it saturates aromatics. Products have a high viscosity index (VI), low pour point, and excellent response to additives.

Catalytic dewaxing and Isodewaxing are discussed in more detail in the second volume of this book.

5.2 Waxes

The raffinate from the solvent extraction unit in a traditional lube plant contains a considerable amount of wax. To recover the wax, the raffinate is mixed with a solvent, usually propane, and cooled in a series of heat exchangers. Further cooling is provided by the evaporation of propane in the chiller and filter feed tanks. The wax forms crystals, which are continuously removed, filtered, and washed with cold solvent. The solvent is recovered by flashing and steam stripping. The wax is purified by heating with hot solvent, after which it is re-chilled, re-filtered and given a final wash.

Paraffin waxes are used to make candles and coated papers for use as bread wrappers, cold-drink cups, and beverage cartons. They are also used in

building materials. The market for packaging is declining, but other uses are on the rise, especially in construction.³¹

5.3 Greases

Greases are made by blending salts of long-chained fatty acids into lubricating oils at temperatures of 400 to 600°F (204 to 315°C). Antioxidants are added to provide stability. Some greases are batch-produced, while others are made continuously. The characteristics of a grease depend to a great extent on the counter-ion (calcium, sodium, aluminum, lithium, etc.) in the fatty-acid salt.

6. ASPHALT PRODUCTION

Asphalt can be produced directly from vacuum residue or by solvent deasphalting (see Section 2.2).

Road-Tar Asphalt. Vacuum residue is used to make road-tar asphalt. To drive off remaining light ends, it is heated to about 750°F (400°C) and charged to a column where a vacuum is applied.

In road-paving, the petroleum residue serves as a binder for aggregate, which can include stone, sand, or gravel. The aggregate comprises about 95% of the final mixture. Polymers are added to the binder to improve strength and durability.

The recommended material for paving highways in the United States is Superpave³² hot-mix asphalt. Superpave was developed in 1987-93 during a US\$50 million research project sponsored by the Federal Highway Administration.

Roofing Asphalt. Roofing asphalt is produced by blowing, which involves the oxidation of asphalt flux by bubbling air through liquid asphalt at 260°C (500°F) for 1 to 10 hours. During this process, organic sulfur is converted to H₂S and SO₂. Catalytic salts such as ferric chloride (FeCl₃) may be used to adjust product properties and increase the rates of the blowing reactions, which are exothermic. To provide cooling, water is sprayed into the top of the blowing vessel, creating a blanket of steam that captures sulfur-containing gases, light hydrocarbons, and other gaseous contaminants. These are recovered downstream. Cooling water may also be sprayed on the outside of the vessel.

The length of the blow depends on desired product properties, such as softening temperature and penetration rate. A typical plant blows four to six batches of asphalt per 24-hour day. There are two primary substrates for roofing asphalt – organic (paper felt) and fiberglass. The production of felt-based roofing shingles consists of:

- Saturating the paper felt with asphalt
 - Coating the saturated felt with filled asphalt
 - Pressing granules of sand, talc or mica into the coating
 - Cooling with water, drying, cutting and trimming, and packaging
- If fiberglass is used as the base instead of paper felt, the saturation step is eliminated.

7. DRYING, SWEETENING, AND TREATING

Drying, sweetening and treating are not as glamorous as extraction and conversion, or even distillation, but they are essential to the performance and safety of finished products. In lubricating oils, traces of olefins and sulfur compounds can form gums and accelerate degradation. At high altitude, excess water in jet fuel can freeze and plug fuel lines. Traces of mercaptans and disulfides in “sour” gasoline can react with water in storage tanks to produce toxic levels of hydrogen sulfide.

7.1 Drying and Sweetening

Light gas streams produced by various refinery units are collected and piped to treating plants, where:

- Propane is recovered for LPG
- Propylene is removed for use in petrochemical plants
- Butanes and butenes are removed for use as alkylation feeds
- Heavier components are recovered and sent to gasoline blending

Knock-out drums collect easy-to-condense liquids, but if necessary drying agents – alumina, silica, or molecular sieves – are used to remove the final traces of water. Some processes use beds of molecular sieves to dry and sweeten at the same time.

Gases containing hydrogen sulfide are scrubbed in trayed contactors with aqueous amines such as diethanolamine (DEA). Hydrogen sulfide is stripped from the “rich” amine with steam and recycled to the contactor. In a properly operating unit, the sweetened gas contains <10 wppm H₂S.

7.2 Treating

Treating improves the odor, color, and stability of straight-run liquids and conversion-unit products. Sulfuric acid treating removes olefins, sulfur, nitrogen, oxygen compounds, and other contaminants. Clay/lime treating of acid-treated oil removes any residual traces of asphaltenes. Caustic treating

with sodium (or potassium) hydroxide removes naphthenic acids, phenols, mercaptans, and H_2S .

If the concentration of organic sulfur exceeds the capacity of a caustic or acid treater, the stream must be sent to a hydrotreater.

8. PRODUCT BLENDING

8.1 Product Specifications

Liquid products from modern refineries comprise several individual streams, which are blended to meet desired specifications. Product specifications developed by ASTM – the American Society for Testing and Materials – are widely used throughout the world. *Table 21* lists some common refinery products along with their ASTM designations.

Table 21. ASTM Specification Numbers for Hydrocarbon Fuels

Product	ASTM Specification	Last Updated	Description
Gasoline	D4814	2003	Standard Specification for Automotive Spark-Ignition Engine Fuel
Jet	D1655	2003	Standard Specification for Aviation Turbine Fuels
Kerosene	D3699	2003	Standard Specification for Kerosene
Diesel	D975	2004	Standard Specification for Diesel Fuel Oils
Fuel Oil	D396	1998	Standard Specification for Fuel Oils

Analogous institutions in other countries – for example, the Japanese Industrial Standards Committee (JISC) and the British Standards Institution (BSI) – serve similar functions. BSI developed the ISO9000 series of standards for managing manufacturing processes.

In addition to setting specifications, these institutions develop and publish test methods used to analyze a wide variety of materials. ASTM and its international cousins cooperate with each other, and they work closely with government regulators. For example, recent low-sulfur gasoline and diesel directives from the U.S. Environmental Protection Agency are incorporated into D975-04 and D4814-03a, respectively.

Other widely used tests and specifications are defined by licensors. For example, UOP's *Laboratory Test Methods*, distributed by ASTM, defines several hundred procedures for analyzing catalysts, chemicals and fuels. Axens (IFP), ChevronTexaco, ExxonMobil and other licensors also distribute test methods to process licensees.

Additives are an essential component of finished fuels. They increase stability, improve flow properties and enhance performance. For example, cetane-improvers are routinely added to diesel fuel, and additives that prevent intake-valve deposits are now required in all grades of gasoline in the United States.

8.2 Gasoline Blending

Forty years ago, making gasoline was a relatively simple task. If a mixture of components met specifications for volatility and octane, it could be shipped to retail outlets and sold as-was. If the octane was low, the problem could be fixed by adding a little tetraethyl lead. Butanes could be added as needed to adjust volatility.

In fact, volatility and octane are still the two most important properties of gasoline. The volatility must be high enough to vaporize during cold weather; otherwise, engines won't start. And octane is still one of the best predictors of performance in a spark-ignition gasoline engine.

8.2.1 Octane Numbers for Hydrocarbons

In a spark-ignition engine, some compounds start to burn before they reach the spark plug. This premature ignition causes knocking, which reduces the power of the engine, increases engine wear, and in some cases causes serious damage.

Octane number is a measure of the propensity of fuels to knock in gasoline engines. It is based on an arbitrary scale in which the octane number of n-heptane is zero and the octane number of isooctane (2,2,4-trimethylpentane) is 100. When a fuel is tested in a standard single-cylinder engine, mixtures of isooctane and n-heptane are used as standards. ASTM D2699 and ASTM D2700 describe methods for measuring research octane number (RON) and motor octane number (MON), respectively. The engine speed for the RON test is 600 rpm, while 900 rpm is used for the MON test. RONC and MONC are sometimes used instead to RON and MON. The "C" stands for clear, which means that the fuel does not contain lead or manganese additives.

Table 22 presents RON and MON values for several pure compounds. Aromatics, olefins, and branched isomers have higher octane numbers than straight-chain isomers with similar carbon numbers. Octane numbers for naphthenes are substantially lower than those for aromatics.

Octane numbers do not blend linearly. For example, while the RON for pure 4-methyl-2-pentene is 99, its blended RON is 130.

In North America, the pump octane of gasoline is the average of RON and MON: $(R+M)/2$. This is the number displayed on pumps at filling stations.

Typical grades are "regular" with a pump octane of 87, "mid-grade" with a pump octane of 89, and "premium" with a pump octane of 91 to 93. In some locales, customers can dial in any octane they want between 87 and 93.

Table 22. Octane Numbers for Selected Pure Compounds

Compound	Type	Formula	RON	MON
n-Butane	n-Paraffin	C ₄ H ₁₀	92	93
n-Pentane	n-Paraffin	C ₅ H ₁₂	62	62
Cyclopentane	Naphthene	C ₅ H ₁₀	101	85
2-Methylbutane	i-Paraffin	C ₅ H ₁₂	92	90
2-Methyl-2-butene	Olefin	C ₅ H ₁₀	97	85
n-Hexane	n-Paraffin	C ₆ H ₁₄	25	26
Methylcyclopentane	Naphthene	C ₆ H ₁₂	91	80
2,2-Dimethylbutane	i-Paraffin	C ₆ H ₁₄	92	93
3-Methyl-2-pentene	Olefin	C ₆ H ₁₂	97	81
4-Methyl-2-pentene	Olefin	C ₆ H ₁₂	99	84
Benzene	Aromatic	C ₆ H ₆	>100	106
n-Heptane	n-Paraffin	C ₇ H ₁₆	-27	0
Methylcyclohexane	Naphthene	C ₇ H ₁₄	75	71
2-Methylhexane	i-Paraffin	C ₇ H ₁₆	42	46
2,2-Dimethylpentane	i-Paraffin	C ₇ H ₁₆	93	96
2,2,3-Trimethylbutane	i-Paraffin	C ₇ H ₁₆	116	101
Toluene	Aromatic	C ₇ H ₈	>100	109
n-Octane	n-Paraffin	C ₈ H ₁₈	<0	<0
Isooctane	n-Paraffin	C ₈ H ₁₈	100	100
2,2,4-Trimethyl-1-pentene	Olefin	C ₈ H ₁₆	>100	86
2,2,4-Trimethyl-2-pentene	Olefin	C ₈ H ₁₆	>100	86
o-, m-, and p-Xylene	Aromatic	C ₈ H ₁₀	>100	100
Ethylbenzene	Aromatic	C ₈ H ₁₀	>100	98

Many refinery streams have the right vapor pressure, boiling range, and octane to end up in the gasoline pool. Table 23 shows properties for stocks recently used to make gasoline in a European refinery. The raffinate came from an aromatics extraction unit, and the pyrolysis gasoline came from a nearby ethylene plant.

Table 23. Gasoline Blend Stock Properties: Example

Component	Density (kg/m ³)	RVP (bar)	Boiling Range		RON	MON
			°C	°F		
Butanes	0.575	3.6	-12 to -0.5	10.4 – 31	97	95
Straight-run Gasoline	0.64	1.15	27 – 80	81 – 176	80.2	76.6
Reformate	0.815	0.08	78 – 197	172 – 387	100.5	89.5
Raffinate	0.685	0.3	65 – 112	149 – 234	60.3	54.5
Hvy FCC Gasoline	0.76	0.2	43 – 185	109 – 365	90.5	79.5
Light FCC Gasoline	0.66	1.3	25 – 89	77 – 192	94.5	81.5
Pyrolysis Gasoline	0.845	0.3	47 – 180	117 – 356	101.5	86.5
Alkylate	0.705	0.3	39 – 195	102 – 383	98	93.5
MTBE	0.746	0.5	48 – 62	118 – 144	115	97

8.2.2 Reformulated Gasoline (RFG)

In 1970, gasoline blending became more complex. The U.S. Clean Air Act required the phase-out of tetraethyl lead, so refiners had to find other ways to provide octane. In 1990, the Clean Air Act was amended. It empowered EPA

to impose emissions limits on automobiles and to require reformulated gasoline (RFG).

Phase I RFG regulations (*Table 24*) required a minimum amount of chemically bound oxygen, imposed upper limits on benzene and Reid Vapor Pressure (RVP), and ordered a 15% reduction in volatile organic compounds (VOC) and air toxics. VOC react with atmospheric NO_x to produce ground-level ozone. Air toxics include 1,3-butadiene, acetaldehyde, benzene, and formaldehyde.

Oxygen can be supplied as ethanol or C₅ to C₇ ethers. The ethers (*Table 25*) have excellent blending octanes and low vapor pressures. This makes them highly desirable gasoline blend stocks. Due to the detection of MTBE in ground water, the future for MTBE is questionable, especially since 1999, when the Governor of California issued an executive order requiring the phase-out of MTBE as a component of gasoline. But in Finland and many other European countries, MTBE is still considered a premium, relatively safe blend stock.³³

Table 24. Simple Model RFG Specifications

Property	Specification
Oxygen, wt%	2.0 max
Benzene, vol%	1.0 max
RVP, Summer	
Class B (psi)	7.2 max
Class B (kPa)	50 max
Class C (psi)	8.1 max
Class C (kPa)	56 max
VOC (summer)	15% reduction
Air toxics	15% reduction
Sulfur	Same as 1990
T90*, olefins, aromatics	Same as 1990

*T90 is the temperature at which 90% of a gasoline blend evaporates.

RFG was implemented in two phases. The Phase I program started in 1995 and mandated RFG for 10 large metropolitan areas. Several other cities and four entire states joined the program voluntarily. In the year 2000, about 35% of the gasoline in the United States was reformulated.

The regulations for Phase II, which took force in January 2000, are based on the EPA Complex Model, which estimates exhaust emissions for a region

Table 25. Blending octane and RVP of ethers and alcohols

Ether or Alcohol	Blending Octane (RON)	Blending RVP (psi)	Blending RVP (kPa)
Methanol	133	58-62	400-427
Ethanol	130	18-22	124-152
Methyl-t-butyl ether (MTBE)	118	8-10	55-69
Ethyl-t-butyl ether (ETBE)	118	3-5	21-34
t-Amyl methyl ether (TAME)	111	1-2	7-14

based on geography, time of year, mix of vehicle types, and – most important to refiners – fuel properties (*Table 26*).

By intent, Phase II is a regulation based on emissions instead of a formula. But refiners don't have to measure the tail-pipe emissions of every gasoline blend. Instead, they can use EPA's computer model – called MOBILE6 – to calculate emissions. By law, complex-model calculations are just as valid as dynamometer tests with vehicles.

Table 26. Example of Product Property Ranges Calculated by the Phase II Complex Model

Property	Reformulated gasoline		Conventional gasoline	
	Low end	High end	Low end	High end
Oxygen	0	3.7	0	3.7
Sulfur	0	500	0	1000
RVP	6.4	10	6.4	11
E200	30	70	30	70
E300	70	95	70	100
Aromatics	10	50	0	55
Olefins	0	25	0	30
Benzene	0	2	0	4.9
MTBE	0	3.7	0	3.7
ETBE	0	3.7	0	3.7
Ethanol	0	3.7	0	3.7
TAME	0	3.7	0	3.7

In practice, blending under the complex model can be less restrictive than blending to a recipe, because changing the amount of one blend-stock (for examples, due to a sudden increase or decrease in availability) can be offset by changes in others.

8.2.3 Gasoline Additives

Table 27 lists the kinds of additives used to prepare finished gasoline. Additive packages vary from season-to-season, region-to-region, and retailer to retailer. “After-market” additives contain similar types of ingredients and usually are more concentrated. They are packaged so that they can be added by consumers to the fuel tanks of individual automobiles.

Table 27. Additives Used in Gasoline

Additive Type	Function
Anti-oxidation	Minimize oxidation and gum formation during storage
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the gasoline supply chain
Anti-icing	Minimize ice in carburetors during cold weather
IVD control (detergent)	Control deposition of carbon on intake valves
CCD control	Control deposition of carbon in combustion chambers
Anti-knock	Methylcyclopentadienyl manganese tricarbonyl (MMT)

8.2.4 Low-Sulfur Gasoline and Ultra-Low-Sulfur Diesel

In recent years, the U.S. Environmental Protection Agency (EPA) and the European Parliament promulgated clean-fuel regulations that are lowering the sulfur content of gasoline and diesel fuel. New sulfur-content standards for several developed countries are shown in *Table 28*, which also shows the target dates for implementation.

Table 28. Clean Fuels: Limits on Sulfur

Fuel Sulfur Content, wppm			
Country	2004 Level	Target Level	Target Date
US ³⁴⁻³⁶			
Gasoline	>300	30	2004 – 2008
Diesel, on-road	500	15	July 1, 2006
	-	-	July 1, 2010
Diesel, off-road	2000 – 3500	500	2007
	-	15	2010
Canada ³⁷			
Gasoline	150	30	2005
Diesel	500	15	2006
Germany ³⁸			
Gasoline	10	10	2003
Diesel	10	10	2003
Sweden ³⁹			
Diesel	10	10	1995
Other EU ³⁸			
Gasoline	150	50	2005
	-	10	2008
Diesel	350	50	2005
	-	10	2008
Australia ⁴⁰			
Gasoline	500	150	2005
Diesel	500	30	2008
Korea (South) ⁴¹			
Gasoline	100	30	2006
Diesel	300	50	2006
Japan ⁴²			
Gasoline	100	10	2008
Diesel	500	50	2004
	-	10	2008

Table 29 shows that, prior to 2004, FCC gasoline was by far the major source of sulfur in gasoline,⁴³ typically accounting for 85 – 95% of the total sulfur in the blending pool.⁴⁴ Obviously, to reduce the sulfur content of gasoline, sulfur either must be kept out of FCC feed or removed from FCC product(s). Both approaches are being used. FCC feed desulfurization is discussed in Section 3.4.2. FCC gasoline post-treating is discussed below.

Table 29. Sources of Sulfur in Gasoline (before 2004)

Component	Contribution to the Gasoline Pool (vol%)	Contribution to Sulfur in the Pool (%)
Alkylate	12	0
Coker naphtha	1	1
Hydrocracker naphtha	2	0
FCC gasoline	36	98
Isomerate	5	0
Light straight-run naphtha	3	1
Butanes	5	0
MTBE	2	0
Reformate	34	0
Total	100	100

8.2.5 FCC Gasoline Post-Treating

Hydrotreating FCC Gasoline. Conventional hydrotreating does a good job of removing sulfur from FCC gasoline. Unfortunately, it also does a good job of reducing octane by saturating C₆-C₁₀ olefins. In recent years, the industry has developed several processes to remove sulfur at minimum octane loss. Licensors include Axens (IFP), CDTECH, ExxonMobil, and UOP.

Sulfur Removal by Selective Adsorption. The ConocoPhillips S Zorb process uses selective adsorption to remove sulfur from FCC gasoline.⁴⁴ The feed is combined with a small amount of hydrogen, heated, and injected into an expanded fluid-bed reactor, where a proprietary sorbent removes sulfur from the feed. A disengaging zone in the reactor removes suspended sorbent from the vapor, which exits the reactor as a low-sulfur stock suitable for gasoline blending.

The sorbent is withdrawn continuously from the reactor and sent to the regenerator section, where the sulfur is removed as SO₂ and sent to a sulfur recovery unit. The clean sorbent is reconditioned and returned to the reactor. The rate of sorbent circulation is controlled to help maintain the desired sulfur concentration in the product.

8.3 Kerosene and Jet Fuel

Kerosene, jet fuel, and turbine fuel have similar boiling ranges. The key product properties are:

- Flash point
- Freezing point
- Sulfur content
- Smoke point

The flash point is the lowest temperature at which a liquid gives off enough vapor to ignite when an ignition source is present. The freezing point is especially important for jet aircraft, which fly at high altitudes where the outside temperature is very low. Sulfur content is a measure of corrosiveness.

The measurement of smoke point goes back to the days when the primary use for kerosene was to fuel lamps. To get more light from a kerosene lamp, you could turn a little knob to adjust the wick. But if the flame got too high, it gave off smoke. Even today, per ASTM D1322, smoke point is the maximum height of flame that can be achieved with calibrated wick-fed lamp, using a wick “of woven solid circular cotton of ordinary quality.”

The smoke point of a test fuel is compared to reference blends. A standard 40%/60% (volume/volume) mixture of toluene with 2,2,4-trimethylpentane has a smoke point of 14.7, while pure 2,2,4-trimethylpentane has a smoke point of 42.8. Clearly, isoparaffins have better smoke points than aromatics.

Table 30 shows specifications for five grades of jet fuel, otherwise known as aviation turbine fuel. The JP fuels are for military aircraft.

Table 30. Specifications for Aviation Turbine Fuels

Specification	Jet A	Jet B	JP-4	JP-5	JP-8
Flash point, °C (min)	38	-	-	60	38
Freeze point, °C (max)	-40 (Jet A) -47 (Jet A-1)	-50	-58	-46	-47
API Gravity	37 – 51	45 – 57	45 – 57	36 – 48	37 – 51
Distillation, °C					
10% max	205	-		205	205
20% max	-	145	145	-	-
50% max	-	190	190	-	-
90% max	-	245	245	-	-
EP	300	-	270	290	300
Sulfur, wt% max	0.3	0.3	0.4	0.4	0.3
Aromatics, vol% max	22	22	25	25	25
Olefins, vol% max	-	-	5	5	5

8.4 Diesel Blending

Diesel blending is simpler than gasoline blending because the limitations are fewer. Only sulfur, cetane number, and (in some countries) aromatics and density are regulated for environmental reasons. Sulfur contributes heavily to particulate emissions from diesel engines, and cetane number is a measure of burning quality in a diesel engine. As with octane number, cetane number measures the tendency of fuels to auto-ignite in a standard test engine. It is easier to start a diesel engine when the cetane number of the fuel is high.

The reference fuels for ASTM D613, which describes the test method for cetane number, are n-cetane, α -methyl-naphthalene, and heptamethylnonane, for which cetane numbers are defined to be 100, 0, and 15, respectively. *Table 31* shows cetane numbers for selected pure compounds.⁴⁵

Table 31. Cetane Numbers for Selected Pure Compounds

Compound	Type	Carbons	Formula	Cetane No.
n-Decane	Paraffin	10	C ₁₀ H ₂₂	76
Decalin	Naphthene	10	C ₁₀ H ₁₈	48
α-Methylnaphthalene	Aromatic	11	C ₁₁ H ₁₀	0*
n-Pentylbenzene	Aromatic	11	C ₁₁ H ₁₆	8
3-Ethyldecane	Paraffin (iso)	12	C ₁₂ H ₂₆	48
4,5-Diethyloctane	Paraffin (iso)	12	C ₁₂ H ₂₆	20
3-Cyclohexylhexane	Naphthene	12	C ₁₂ H ₂₄	36
Biphenyl	Aromatic	12	C ₁₂ H ₁₀	21
α-Butylnaphthalene	Aromatic	14	C ₁₄ H ₁₆	6
n-Pentadecane	Paraffin	15	C ₁₅ H ₃₂	95
n-Nonylbenzene	Aromatic	15	C ₁₅ H ₂₄	50
n-Hexadecane (cetane)	Paraffin	16	C ₁₆ H ₃₄	100*
2-Methyl-3-cyclohexylnonane	Naphthene	16	C ₁₆ H ₃₄	70
Heptamethylnonane	Paraffin (iso)	16	C ₁₆ H ₃₄	15*
8-Propylpentadecane	Paraffin (iso)	18	C ₁₈ H ₃₈	48
7,8-Diethyltetradecane	Paraffin (iso)	18	C ₁₈ H ₃₈	67
2-Octylnaphthalene	Aromatic	18	C ₁₈ H ₂₄	18
n-Eicosane	Paraffin	20	C ₂₀ H ₄₂	110
9,10-Dimethyloctane	Paraffin (iso)	20	C ₂₀ H ₄₂	59
2-Cyclohexyltetradecane	Naphthene	20	C ₂₀ H ₄₀	57

* Used as a standard for ASTM D976

Cetane index, as defined by ASTM D976, is not a measurement, but the result of a calculation based on density and mid-boiling point. It is nearly the same as the cetane number for diesel fuels comprised mostly of straight-run gas oils blended with lesser amounts of cracked stocks. Diesel index is a simpler calculation based on density and aniline point. The streams listed in Table 32 are typical candidates for making diesel fuel.

Table 32. Properties of U.S. Diesel Blend Stocks, Year 2000 (California Excluded)⁴⁶

Blend Stock	Percent of Total U.S. Pool	Sulfur (wt%)	API Gravity	Cetane (no additives)
Straight-run gas oil	12.4	0.222	30.3 – 42.2	40.3 – 45.0
Hydrotreated straight-run	51.9	0.036	29.9 – 42.9	44.5 – 50.4
FCC light cycle oil	3.1	0.532	22.3 – 33.1	<<30
Hydrotreated light cycle oil	19.4	0.087	30.7 – 45.0	42.7 – 44.1
Coker gas oil	1.0	0.342	32.3 – 42.4	<<30
Hydrotreated coker gas oil	8.2	0.026	29.9 – 34.8	36.1 – 45.3
Hydrocrackate	4.0	0.008	32.9 – 41.8	50.2

Table 33 presents clean-diesel specifications for the European community, which were based on two extensive research programs – Auto Oil I and Auto Oil II. Automobile manufacturers, oil refining companies, and government agencies participated in both programs. Auto Oil I lasted four years, from 1992 to 96. Auto Oil II was launched in 1997, and the final report was issued in October 2000. The purpose of the programs was to find ways to reduce emissions from gasoline and diesel-powered vehicles, considering public health, technology and economics.

Table 33. EU Specifications for Automotive Diesel

Specification	Units	Year 2000 Limits	Possible Future Limits
Cetane number		51 (min)	55 (min)
Cetane index		No spec	52 (min)
Density @ 15°C	g/cm ³	0.845 (max)	0.84
Distillation			
90% boiling point	°F	no spec	608 (max)
95% boiling point	°F	680 (max)	644 (max)
Final boiling point	°F	no spec	662 (max)
90% boiling point	°C	no spec	320 (max)
95% boiling point	°C	360 (max)	340 (max)
Final boiling point	°C	no spec	350 (max)
Polyaromatic hydrocarbons (PAH)	wt%	11 (max)	2 (max)
Total aromatics	wt%	no spec	15 (max)
Sulfur	wppm	350 (max)*	10 (max)

- As discussed elsewhere, diesel sulfur will be limited to 50 wppm in 2005.

Catalytic converters led to the elimination of lead from gasoline, because lead poisons the converter catalyst. Similarly, sulfur poisons catalysts that may be used on future vehicles. Hence, the reduction of sulfur in gasoline and diesel fuel to ultra-low levels is a key requirement of Auto Oil II.

Around the world, the transportation and fungibility of ultra-clean fuels is a major concern. For common-carrier pipelines, which transport various products made by different refiners, cross-contamination is a major concern. The interface layer between shipments is called “trans mix.” If a shipment of gasoline containing 30 wppm of sulfur follows a batch of diesel containing 500 wppm of sulfur, the sulfur-contaminated trans mix could comprise more than 20% of the gasoline. Consequently, several pipeline companies have announced that in the future they will not transport any high-sulfur material.

Other important diesel-fuel properties include flash point, cloud point, pour point, kinematic viscosity, and lubricity. Cloud point and pour point indicate the temperature at which the fuel tends to thicken and then gel in cold weather. In addition to providing energy, diesel fuel also serves as a lubricant for fuel pumps and injectors, which prolongs the life of the engine. Viscosity measures the tendency of a fluid to flow. In a diesel engine, viscosity indicates how well a fuel atomizes in spray injectors. It also measures its quality as a lubricant for the fuel system. Lubricity measures the fuel’s ability to reduce friction between solid surfaces in relative motion. It indicates how the engine will perform when loaded.

8.4.1 Diesel Additives

Chemical additives improve the performance and extend the tank-life of diesel fuels. Typical types of additives are shown in Table 34.

Table 34. Additives Used in Diesel Fuel

Additive Type	Function
Anti-oxidation	Minimize oxidation and gum formation during storage
Cetane improvement	Increase cetane number
Dispersion	Improve behavior in fuel injectors
Anti-icing	Minimize ice formation during cold weather
Detergent	Control deposition of carbon in the engine
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the diesel fuel supply chain
Cold-flow improvement	Improve flow characteristics in cold weather

9. PROTECTING THE ENVIRONMENT

The ways in which the refining industry protects the environment are discussed in more detail in Chapter 14, Environmental Pollution Control. In this section, we provide a brief overview of the methods used to improve air quality, prevent water pollution, and dispose of solid wastes.

9.1 Air Quality

In the 1970s and 1980s, environmental laws compelled refineries to reduce emissions of SO_x, NO_x, CO₂, and hydrocarbons. In the atmosphere, SO_x reacts with water vapor to make sulfurous and sulfuric acids, which return to earth as acid rain. Volatile hydrocarbons react with NO_x to make ozone. CO₂ is a major “green-house” gas. To reduce these pollutants, the industry tightened its operation by:

- Reducing fugitive hydrocarbon emissions from valves and fittings
- Removing sulfur from refinery streams and finished products
- Adding tail-gas units to sulfur recovery plants
- Reducing the production of NO_x in fired heaters
- Scrubbing SO_x and NO_x from flue gases
- Reducing the production of CO₂ by increasing energy efficiency

9.1.1 Sulfur Recovery

Conversion processes, hydrotreaters, and sweetening units remove chemically bound sulfur from petroleum fractions. That’s a good thing, but where does the sulfur go? The answer depends upon the form in which it is produced.

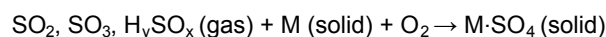
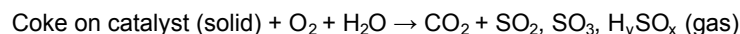
SO_x Abatement. Fuel-oil fired heaters and the regenerators of FCC units are major sources of refinery SO_x and NO_x emissions. The most obvious way to reduce SO_x emissions from a heater is to use low-sulfur fuels. Unfortunately, although that solution requires no investment, it is probably

the most expensive due to the relatively high cost of buying low-sulfur fuel oil or hydrotreating high-sulfur fuel oil.

A large fraction of the sulfur in the feed to an FCC unit ends up in coke on the catalyst. SO_x is formed in the regenerator when the coke is burned away. Therefore, removing sulfur from the feed decreases SO_x emissions.

As stated in Section 3.4.2, using a hydrotreater or hydrocracker for feed HDS eliminates or minimizes the cost of post-FCC desulfurization equipment. Removing basic nitrogen decreases deactivation of acid sites on the FCC catalyst, which allows the FCC to reach a given conversion at lower temperatures. The saturation of aromatics in the feed pretreater provides the biggest benefit, because it converts hard-to-crack aromatics into easier-to-crack naphthenes. This alone can justify the installation of an FCC feed pretreater. Therefore, in addition to abating SO_x, hydrotreating the feed to an FCC can generate a substantial return.⁴³

FCC Regenerator (Oxidizing Environment)



FCC Riser/Reactor (Reducing Environment)

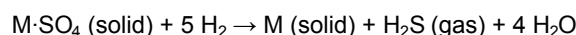


Figure 25. Mechanism of SO_x transfer in FCC units.

SO_x Transfer Additives. Arguably, SO_x transfer additives are the most cost-effective way to lower SO_x emissions in an FCC unit. These materials, first developed by Davison Chemical, react with SO_x in the FCC regenerator to form sulfates (Figure 25). When the sulfated additive circulates to the riser/reactor section, the sulfate is reduced to H₂S, which is recovered by amine absorption and sent to the sulfur plant. In some units, these additives reduce FCC SO_x emissions by more than 70%. Consequently, if a pre-treater or post-treater still must be installed, its size can be reduced.

Flue-Gas (Stack-Gas) Scrubbing. Flue-gas scrubbing is a refiner's last chance to keep NO_x and SO_x out of the air. In wet flue-gas desulfurization, gas streams containing SO_x react with an aqueous slurry containing calcium hydroxide Ca(OH)₂ and calcium carbonate CaCO₃. Reaction products include calcium sulfite (CaSO₃) and calcium sulfate (CaSO₄), which precipitate from the solution.

NO_x removal is more difficult. Wet flue-gas scrubbing removes about 20% of the NO_x from a typical FCC flue gas. To remove the rest, chemical reducing agents are used. In the Selective Catalytic Reduction (SCR) process, anhydrous ammonia is injected into the flue gas as it passes through a bed of

catalyst at 500 to 950°F (260 to 510°C). The chemical reaction between NO_x and ammonia produces N₂ and H₂O.

Hydrogen Sulfide Removal. When sulfur-containing feeds pass through hydrotreaters or conversion units, some or most of the sulfur is converted into H₂S, which eventually ends up in off-gas streams. Amine absorbers remove the H₂S, leaving only 10 to 20 wppm in the treated gas streams. H₂S is steam-stripped from the amines, which are returned to the absorbers. The H₂S goes to the refinery sulfur plant.

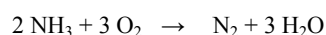
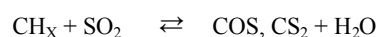
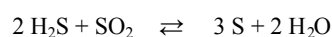
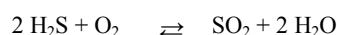


Figure 26. Claus reactions.

Claus Sulfur Recovery Process. At the sulfur plant, H₂S is combined with sour-water stripper off-gas and sent to a Claus unit. Invented in 1881 by Carl Freidrich Claus,⁴⁷ almost every refinery in the world uses some version of this process to convert H₂S into elemental sulfur. A simplified version of Claus-reaction chemistry is shown in Figure 26.

Figure 27 shows a process schematic for a Claus unit. H₂S and a carefully controlled amount of air are mixed and sent to a burner, where about 33% of the H₂S is converted to SO₂ and water. From the burner, the hot gases go to a reaction chamber, where the reactions shown in Figure 26 reach equilibrium. In several units, the air is enriched with oxygen to increase plant capacity.

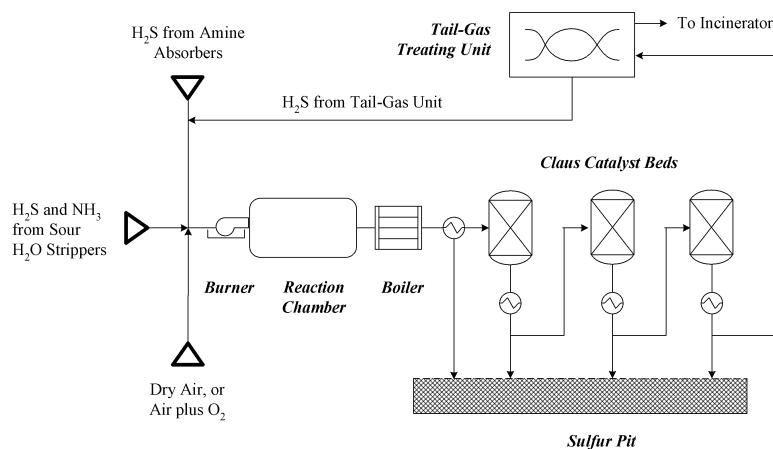


Figure 27. Claus process.

As shown, elemental sulfur is produced by the reversible reaction between SO_2 and H_2S . COS and CS_2 appear in small amounts, but even traces of these compounds are hard to remove in tail-gas treating units. Ammonia comes in with the sour-water stripper off-gas. In the Claus process, it is thermally decomposed into nitrogen and water.

In the Claus burner, combustion temperatures reach 2200°F (1200°C). Needless to say, this generates a tremendous amount of heat. Much of the heat is recovered in a waste-heat boiler, which generates steam as it drops the temperature to 700°F (370°C).

Next, the process gas goes to a condenser, where it is cooled to about 450°F (232°C). At this temperature, sulfur vapors condense, and the resulting molten sulfur flows through a drain to a heated sulfur-collection pit. At the bottom of the drain, a seal leg maintains system pressure and keeps unconverted gases out of the pit.

Uncondensed sulfur and other gases flow to a series of catalyst beds, which recover additional sulfur by promoting the reaction between left-over H_2S and SO_2 . With fresh catalyst and a stoichiometric gas composition, the cumulative recovery of sulfur after the four condensers is about 50%, 80%, 95%, and 96-98%, respectively.

Tail-gas treating units (TGTU) bring the total sulfur recovery up to $>99.9\%$. Most tail-gas treating processes send the tail gas to a hydrotreater, which converts all sulfur-containing compounds (SO_2 , SO_3 , COS , CS_2 and S_x) into H_2S . In the SCOT process, offered by Shell Global Solutions, the H_2S is absorbed by an amine and returned to the front of the Claus furnace. In the LO-CAT[®] process, offered by Merichem, H_2S is air-oxidized to sulfur in an aqueous solution containing a chelated iron catalyst.

For all tail-gas treatment processes, the last traces of unrecovered sulfur go to an incinerator, where they are converted into SO_2 and dispersed into the atmosphere.

9.2 Waste Water Treatment

Waste water treatment is used to purify process water, runoff, and sewage. As much as possible, purified waste-water streams are re-used in the refinery. Wastewater streams may contain suspended solids, dissolved salts, phenols, ammonia, sulfides, and other compounds. The streams come from just about every process unit, especially those that use wash water, condensate, stripping water, caustic, or neutralization acids.

9.2.1 Primary Treatment

Primary treatment uses a settling pond to allow most hydrocarbons and suspended solids to separate from the wastewater. The solids drift to the

bottom of the pond, hydrocarbons are skimmed off the top, and oily sludge is removed. Difficult oil-in-water emulsions are heated to expedite separation.

Acidic wastewater is neutralized with ammonia, lime, or sodium carbonate. Alkaline wastewater is treated with sulfuric acid, hydrochloric acid, carbon dioxide-rich flue gas, or sulfur.

9.2.2 Secondary Treatment

Some suspended solids remain in the water after primary treatment. These are removed by filtration, sedimentation or air flotation. Flocculation agents may be added to consolidate the solids, making them easier to remove by sedimentation or filtration. Activated sludge is used to digest water-soluble organic compounds, either in aerated or anaerobic lagoons. Steam-stripping is used to remove sulfides and/or ammonia, and solvent extraction is used to remove phenols.

9.2.3 Tertiary Treatment

Tertiary treatment processes remove specific pollutants, including traces of benzene and other partially soluble hydrocarbons. Tertiary water treatment can include ion exchange, chlorination, ozonation, reverse osmosis, or adsorption onto activated carbon. Compressed oxygen may be used to enhance oxidation. Spraying the water into the air or bubbling air through the water removes remaining traces of volatile chemicals such as phenol and ammonia.

9.3 Solid Waste

Refinery solid wastes may include the following materials:

- Spent catalyst and catalyst fines
- Acid sludge from alkylation units
- Miscellaneous oil-contaminated solids

All oil-contaminated solids are treated as hazardous and sent to sanitary landfills. Recently, super-critical extraction with carbon dioxide has been used with great success to remove oil from contaminated dirt.

10. POWER, STEAM, HYDROGEN, AND CO₂

Utilities are a critical ingredient in petroleum processing. After excluding the cost of crude oil and other raw materials, power and steam account for almost half of a refinery's operating costs.

Due to clean-fuel regulations, many refineries are implementing hydrogen recovery/purification projects and/or installing steam/hydrocarbon reformers to generate on-purpose hydrogen.

10.1 Power

Refineries purchase electricity from outside sources, but they also produce much of their own power with steam turbines or gas engines. Electrical substations distribute power throughout the facility. For safety reasons, substations are located far away from sources of combustible vapors.

10.2 Steam

Steam production and distribution systems are quite complex, involving 3 to 4 different steam qualities and hundreds of pipes and valves. Cooling towers and evaporators are used to dispose of unused steam.

Steam is generated by boilers and heat-producing process units. FCC units, Claus units, and steam/hydrocarbon reformers (hydrogen plants) are major sources of refinery steam.

Steam boilers are fired with refinery fuel gas, natural gas, and/or fuel oil. Fuel oil is a blend of residual oils with flow-improving cutter stocks. Usually, it is pumped through a series of strainers before being burned.

Refinery fuel gas is collected from process units, sweetened in amine absorbers, and sent to a balance drum. Natural gas and LPG may be used to augment the fuel gas supply, and to replace it when needed. The balance drum stabilizes system pressure and calorific content. It also provides a place for suspended liquids to separate from the gas.

Boiler feedwater (BFW) is used for steam generation. BFW must be free of contaminants, because salts and dissolved gases, particularly CO₂ and O₂, can cause extensive corrosion.

10.3 Hydrogen and CO₂

Due to the extra hydrotreating required by clean-fuel regulations, refiners are looking for additional sources of hydrogen, which can be recovered from off-gas streams or generated by new hydrogen plants. Chapter 26 by Nick Hallale, Ian Moore and Dennis Vauk describes a methodology for optimizing hydrogen recovery from existing refinery hydrogen networks. For new hydrogen plants, steam-hydrocarbon reforming is used. This process is described in detail in Chapter 25 by Andrew Crews and Gregory Shumake and in the Chapter 24 by Milo Meixell. A brief overview is given in this section.

The feed gas for a steam-hydrocarbon reformer can be natural gas, refinery off-gas, or a mixture of the two. The feed gas is desulfurized, mixed with

superheated steam and sent through tubes packed with a nickel-based catalyst. Reaction temperatures are very high – 1100 to 1600°F (593 to 871°C).

The reformed gas, which contains water vapor, H₂, CO, and CO₂, is sent through a high-temperature shift (HTS) converter. In the HTS converter, carbon monoxide reacts with steam over an iron-based catalyst to form additional CO₂ and hydrogen.

In modern units, the CO₂ and residual CO and CH₄ are removed by pressure-swing adsorption (PSA). As an option, residual CO is converted to methane in a hydrotreater.

In older units, CO₂ is removed with an absorber containing an amine, Sulfinol[®], Rectisol[®] or by the Benfield[™] process, which uses hot potassium carbonate. Recovered CO₂ can be sold as a product.

11. REFINING ECONOMICS

11.1 Costs

The purchase of crude oil and external blend stocks accounts for about 85% of a refinery's operating costs. About half of the remaining 15% is due to energy in the form of fuel and electrical power. Table 35 shows a typical breakdown of plant-wide operating costs. For the refining industry, labor costs are about 2.3% of sales compared to 7.6% for making automobile bodies, 8.3% for plastics, and 12.7% for computers.⁴⁸

About half of the energy used by a refinery is generated from crude oil. In Table 35, crude oil used for energy production is included with "Crude oil and blend stocks." Corporate overhead, interest payments, taxes, and capital depreciation are not included in this analysis.

Table 35. Typical breakdown of refinery operating costs.

Item	Percent of "Other"	Percent of Total
Crude oil and blend stocks	–	85
Other operating costs		
Fuel oil, fuel gas	40.7	6.1
Electrical power	5.3	0.8
Maintenance	23.3	3.5
Operations	18	2.7
Catalysts and chemicals	12.7	1.9
Totals	100	100

Ultimately, prices for crude oil are set by members of the Organization of Petroleum Exporting Countries (OPEC), which are listed in Table 36. The members of OPEC supply about 40% of the world's oil production and own

about 75% of the world's proven oil reserves; consumption within OPEC is very low, so almost all of the produced oil is exported.

Table 36. OPEC Oil Reserves and Production⁴⁹

Country	Daily Production, 2002 (million barrels)	Proven Reserves, 2003 (billion barrels)
Algeria	1.58	9.2
Indonesia	1.35	5.0
Iran	3.53	89.7
Iraq	2.04	112.5
Kuwait	2.02	96.5
Libya	1.38	29.5
Nigeria	2.12	24.0
Qatar	0.84	15.2
Saudi Arabia	8.71	261.8
United Arab Emirates	2.38	97.8
Venezuela	2.91	77.8

Figure 28 illustrates how oil prices have changed since 1861.⁵⁰ The bottom trend shows the actual historical prices. The top trend converts the historical prices into 2002 dollars. The big spikes in 1973 and 1978-81 correspond to actions taken by the OPEC cartel. In 1973, the first Arab Oil Embargo caused the average price of oil to rise from about US\$4 per barrel to more than US\$10 per barrel. In 1978, the revolution in Iran triggered another steep increase in prices, which peaked in 1981 at about US\$38 per barrel.

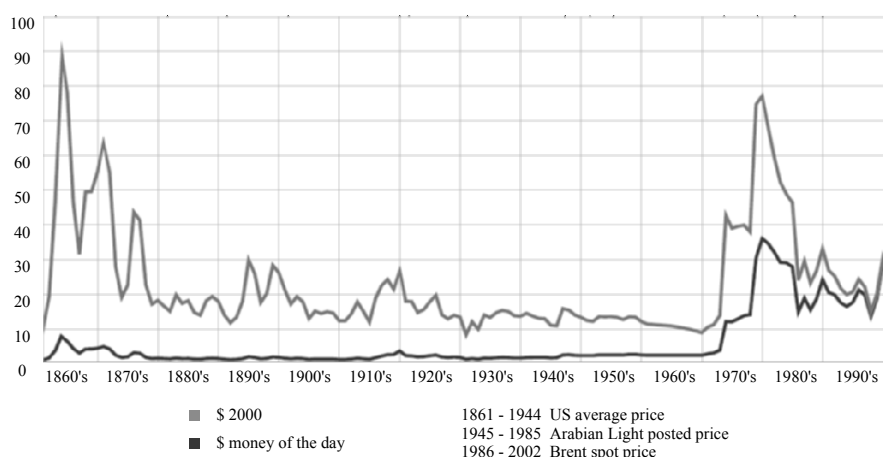


Figure 28. Oil Prices Since 1861 (\$US)

In response to these severe price increases, major oil-consuming countries developed alternatives and implemented energy conservation measures. The member countries of OEDC (Organization for Economic Co-operation and Development) decreased oil demand from 44 million b/d in 1979 to 37

million b/d in 1985. Significantly, France now gets more than 75% of its electricity from nuclear power plants, and most of the rest is hydroelectric.

Slowly but steadily, oil consumption rose from 58 million b/d in 1983 to 75 million b/d in 2002. Most of the rise came from developing countries (*Figure 29*). The price run-up in 2003-05 was caused by increased rates of rising demand in China and India, whose economies were booming. At the same time, there was an (apparent) inability of exporters to keep pace with demand and a lack of spare refining capacity, especially in North America.

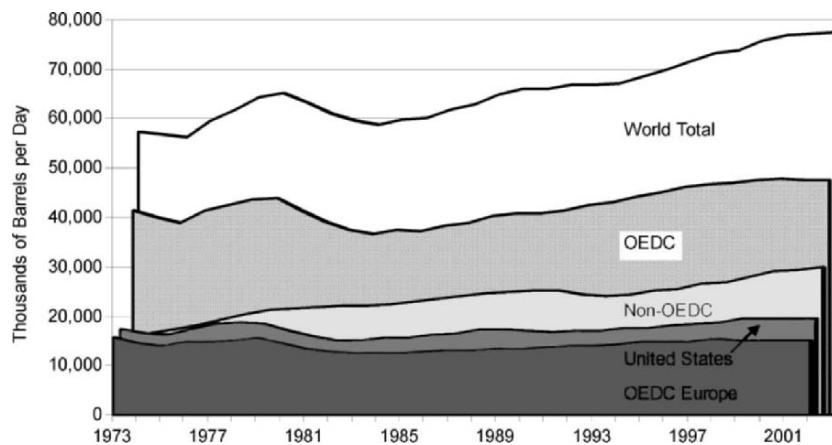


Figure 29. Worldwide Petroleum Processing Capacity Since 1973

Sudden changes in consumption, either up or down, are unlikely due to the long lead-time needed to increase population, build new refining capacity, build plants that produce energy from alternative sources, or implement energy conservation measures. It takes 18 to 24 months to design and install a new crude distillation unit. Alternative energy production plants take a lot longer, especially in the United States, where it takes years to obtain permits for a new plant of significant size.

“Everybody wants power, but nobody wants a power plant in his yard.”

In contrast, supply can change overnight – at least in the minds of oil traders.

11.2 Revenues

The economics of some important conversion units are summarized in Table 37. In each case, one major contributor accounts for most of the operating costs. Hydrotreating is an “enabling” process with low margins, but it is essential to the proper functioning of many other units in a refinery.

Table 37. Economics for Selected Conversion Units.

Process	Operating Costs (US\$ per bbl)	Major Cost Factor	Percent of Total Cost	Net margin (\$US per bbl)
FCC	2.0 – 2.2	Fuel	70	4.0 to 5.0
Cat. Reforming	3.0	Utilities	90	2.0 to 2.5
Alkylation	4.8 – 5.5	Utilities	65 to 75	3.5 to 4.5
Hydrotreating	1.7	Hydrogen	60 to 70	0.5
Hydrocracking	4.0 to 4.5	Hydrogen	75 to 80	1.5 to 3.0

11.3 Margins

Refinery margins depend on location, size, automation, complexity, and crude and product prices. A good indicator of margins is the “crack spread” – the difference in price between crude oil and refined products.

11.3.1 Location, Location, Location

A well-located refinery has lower operating costs and increased operating flexibility. When located near other refineries and petrochemical plants in a coastal industrial basin such as Rotterdam, the Houston Ship Channel, etc., it has access to a wide variety of crudes, blend stocks, transportation options, additives, supplies, and services. This enhances its ability to cope with upsets and to react aggressively to sudden changes in price differentials.

In a basin, the infrastructure – seaports, pipelines, laboratories, waste-handling facilities – is extensive. Often, a single large supplier provides utilities and commodities such as hydrogen to several different customers, reducing costs for all concerned. This is because, due to economies of scale, production and distribution costs for a large plant are lower than those for multiple smaller plants with equivalent total capacity.

As long as space is available, industrial basins tend to grow. They also attract and support large pools of operators and engineers. Contractors, who perform as-needed engineering, maintenance, and other important service work, also are attracted by “basin gravitation.”

Lest we leave you with the idea that non-basin facilities are inherently handicapped, we should emphasize that other locations also can have advantages. For example, the ConocoPhillips refinery in Borger, Texas was built in 1932 in an area that still produces large quantities of natural-gas liquids. Except for a few nearby chemical plants, the Borger refinery seems isolated. However, it is connected by pipelines to the U.S. Gulf Coast and to the mammoth hub of pipelines in Cushing, Oklahoma. Through these various pipelines, the Borger complex receives crude oil from the Texas Gulf Coast and supplies products to Houston, Denver, Kansas City, and beyond. Also, in

addition to gasoline and other fuels, it produces a large number of ultra-pure chemicals, some of which are not manufactured in quantity anywhere else in the United States.

11.3.2 Size

Size isn't everything, but it certainly helps. On a per-ton basis, it costs less to design and build large process units. Engineering costs are essentially capacity-independent. This economy of scale translates into higher returns on investments, faster paybacks, and/or reduced interest payments as percentages of total project costs.

Similarly, bigger plants have lower per-barrel operating costs because many fixed costs, especially labor, are nearly size-independent.

Size and weight determine the maximum size of for the vessels in large process units. High-pressure reactors can only be built in a few special factories in Italy and Japan. They can weigh more than 2200 tons and their diameters may exceed 15 feet (5 meters), but it must be possible to move them over existing road and to lift them with available cranes.

11.3.3 Conversion Capability and Complexity

The most profitable refineries tend to be more complex. In the 1960s, W.L. Nelson developed an index for calculating the relative costs of refineries based on complexity.⁵¹ *Table 38* presents complexity indices for individual processes, and *Table 39* compares complexity in different parts of the world.

Table 38. Nelson Complexity Indices for Individual Process Units

Process Unit	Complexity Index
Crude distillation	1
Vacuum distillation	2
Visbreaking	2.75
Delayed and fluid coking	6
FCC	6
Catalytic reforming	5
Hydrotreating	2-3
Hydrocracking	6
Alkylation, polymerization	10
Aromatics, isomerization	15
Lubes	10
Asphalt	1.5
Hydrogen production	1

To compute the Nelson Index for a given refinery or regions, the complexity factors for each individual unit is multiplied by the percentage of the incoming crude that it processes. The individual unit results are summed to give a total plant complexity rating.

Table 39. Nelson Complexity Indices for Selected Regions

Region	Refineries	Throughput (million bpcd)	Complexity Index
C.I.S.	58	10.0	3.8
Latin America	80	6.3	4.7
Asia	135	14.7	4.9
Europe	116	14.5	6.5
Canada	23	1.8	7.1
United States	153	15.3	9.5

In short: The petroleum refining business is highly capital-intensive and competition is fierce. The predominant cost – purchase of crude oil – is beyond a refiner’s control, due to the fact that crude-oil costs are, for the most part, determined by OPEC. Even so, large, well-located, high-conversion refineries can be very profitable, especially during spikes in product prices. In 2005, crack spreads reached all-time highs, exceeding \$15 per barrel in most of the United States and >\$20 per barrel in California.

11.3.4 Automation

As discussed in Chapter 22, model-predictive control (MPC) and real-time optimization (RTO) can improve the profitability of a major conversion unit by 5 to 10%. Refinery-wide, benefits from MPC and RTO can exceed US\$0.40 per barrel, or \$US30 million per year for a high-conversion 200,000 b/d refinery.

12. SAFETY, RELIABILITY, AND MAINTENANCE

This section could have been a part of Section 11: Refining Economics, because the most profitable refineries are also the safest and most reliable. Just consider this: For a 200,000 barrels-per-day refinery, a minor accident that shuts down the plant for just one week can cost US\$3 to 6 million in lost revenue. An accident that damages a major conversion unit can cost between US\$80 and US\$120 million in lost revenue during the 12-18 months required for reconstruction, plus US\$20 to 50 million (or more) in reconstruction expenses. These estimates don’t include the cost of repairing damage to the surrounding community. To settle lawsuits and pay penalties for a “minor” incident that occurred in 1994, a California refiner paid more than US\$83 million.⁵²

12.1 Refinery Staffing

Figure 30 shows a typical refinery organization chart.

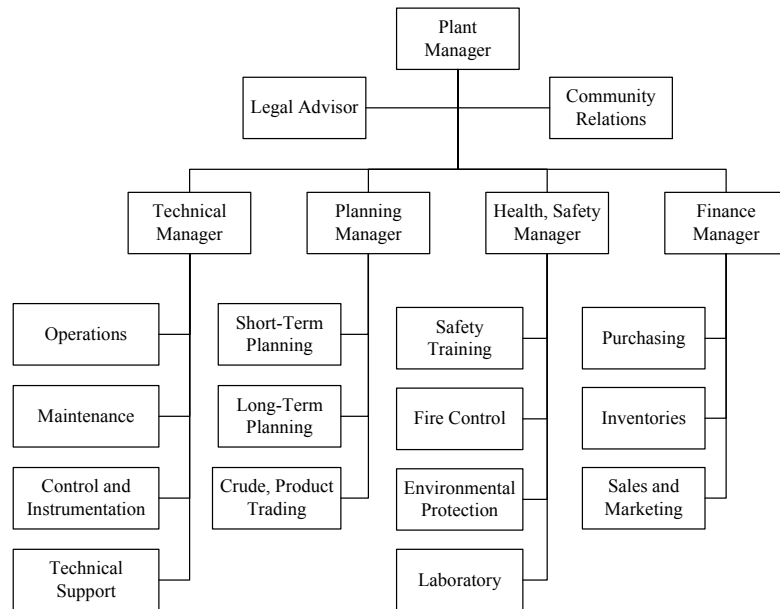


Figure 30. Refinery Organization Chart

More than anything else, safety and reliability depend on people who work in a plant. A typical U.S. or Canadian refinery employs 500 to 750 people. About half of these are operators and 20 to 25% are engineers.

12.2 Safety

“Safety first!”

“Safety is a state of mind.”

“All accidents are preventable.”

In safely operated plants, these maxims are emphasized over and over again to each and every employee. Industry studies show that safe plants share the following characteristics:

- Top managers demonstrate personal commitment to safety.
- Safety goals are aggressive. A perfect example of an aggressive goal is “Zero Lost-Time Accidents.”
- Safe performance is rewarded. For achieving aggressive safety goals, individual workers can receive thousands of dollars per year.
- Safety takes priority over (false) economics. In safety-first plants, operators are encouraged to shut a unit down at the first sign of serious trouble. Historically, far too many incidents are caused (or aggravated) by someone who decides to keep running a unit despite indications that something is wrong.⁵²

- Protective clothing is required. Anyone in an operations area must wear fire-proof coveralls, a helmet, and safety goggles. Hearing protection and steel-toed shoes may also be required.
- Safety equipment is well-maintained and readily available. Safety equipment includes alarms, intercoms, sprinkler systems, self-contained breathing units, and first-aid kits.
- Safety training is rigorous and continuous. Training topics include:
 - **Safety regulations.** In the United States, safety regulations are issued and enforced by the Occupational Safety and Health Administration (OSHA). Per OSHA requirements, for every chemical in the plant, a Material Safety Data Sheet (MSDS) must be available. An MSDS describes the substance, classifies its danger, if any, and describes proper storage and handling.
 - **Emergency procedures,** including where to go and what to do when they hear different alarms. Usually, there are at least two kinds of alarm sounds – a fire alarm and a toxic-release alarm. Possible toxic releases include H₂S, which is actually more poisonous than hydrogen cyanide, and carbon monoxide.
 - **Maintenance safety.** Historically, most refinery accidents occurred during maintenance. Now, all proposed maintenance work is reviewed and pre-approved by operations, engineering, craftspeople and management. Lock-out, tag-out procedures prevent unsuspecting employees from trying to start equipment that shouldn't be started.
- Contractors must be trained, too. Before they can enter the plant, all contractors are required to complete safety training.

Safety programs work! For example, a report by ChevronTexaco claims that, between 1990-91 and 2000-01, safety programs reduced injuries by 90% at its large refinery in Pascagoula, Mississippi.⁵³ In 2003, Valero's Paulsboro refinery had no lost-time injuries and a total recorded injury rate of 0.7, which is three times better than the industry average. For this and other achievements, the refinery was one of only 13 in the United States to be honored as "Star Site" within OSHA's Voluntary Protection Program (VPP). In addition, the plant earned four national safety awards from the National Petroleum Refiners Association (NPRA). "Our successful VPP efforts have taken the commitment of every person in this refinery, and I'm proud of how everybody has worked together as a team to make it a safety leader," said Mike Pesch, vice president and manager of the refinery.⁵⁴

12.3 Reliability and Maintenance

Most refinery maintenance takes place during scheduled shut-downs, when refinery personnel, often with help from contractors, clean, inspect, maintain and (if necessary) repair equipment.

During a major turnaround, process vessels are drained and filled or blanketed with nitrogen gas. In conversion units, catalysts are unloaded and the reactors are metallurgically “pacified” with chemicals such as aqueous sodium carbonate. The process units are inspected, and pre-planned revamps are implemented. Reactors are re-loaded, either with fresh or regenerated catalysts, and the unit is re-started.

Maintenance planning is complex. Complete planning and competent management are prerequisites to success.⁵⁵

13. PETROLEUM PROCESSING TRENDS

13.1 Industry Consolidation

The oil industry has been consolidating since oil prices exploded during 1978-81, after the revolution in Iran. According to the United States Energy Information Administration,⁵⁶ in 1981 there were 324 refineries in the United States (*Figure 31*). Ten years later, there were 202, and by the end 2002 there were 153. Interestingly, during that same time-frame, the total capacity dropped from 18.6 million b/d to a low of 15.0 million b/d in 1994. It then climbed back to 16.8 million b/d by the end of 2002. The average capacity nearly doubled, from 57,400 b/d in 1981 to 109,700 b/d in 2002.

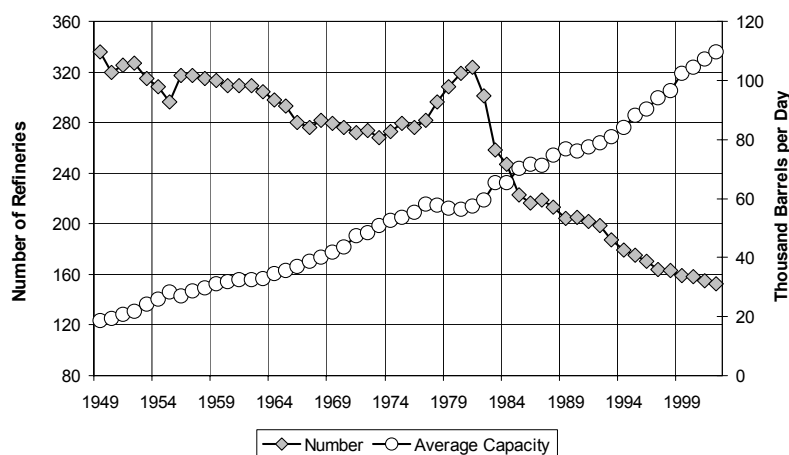


Figure 31. Average Capacity of U.S. Refineries 1949-2002

It's tempting to conclude that 171 refineries were shut down during the past 20-plus years and the remaining plants got a whole lot bigger. Indeed, there were a lot of shut-downs and expansions, but that's not the whole story. In many cases, mergers between neighbors decreased the apparent number of

plants without affecting capacity, because equipment from both predecessors continues to run at full rate. For example, the 300,000 b/d Flint Hills refinery in Corpus Christi, Texas used to be three separate plants owned by Koch Refining, Gulf States and Kerr-McGee.

Trends are similar in Western Europe. Total capacity has levelled off, but the number of refineries has decreased, in part due to mergers. Plants owned by BP and Texaco were merged to form the 380,000 b/d Netherlands Refining Company (NeRefCo). MiRO, a 283,000 b/d refinery in Karlsruhe, Germany, was created by a merger between refineries owned by Esso and by the by the four OMW partners – DEA, Conoco, Veba, and Petroleos de Venezuela.

In recent years, consolidation has evolved from relatively small mergers between neighboring refineries into mega-mergers between fully integrated oil corporations. Many of these are listed in *Table 40*.

Table 40. Large Mergers and Acquisitions in the Oil Industry

Present Name	Component Parts
BP	BP, Amoco, Arco, Castrol, Veba
ChevronTexaco	Chevron, Texaco, Gulf
ConocoPhillips	Conoco, Phillips, Tosco, Unocal
ExxonMobil	Exxon, Mobil
Total	Total, Fina, Elf
Valero	Valero, Phibro, Diamond Shamrock, Premcor, Ultramar*

*Valero acquired its Paulsboro refinery from Mobil and its Benicia refinery from Exxon

13.2 Environmental Regulations

A second main trend in petroleum processing – tightening environmental regulations – started in 1970 and accelerated in recent years. Major areas of improvement include:

- Reduced fugitive emissions. This requires modification or replacement of valves and compressor seals, along with more-vigilant maintenance.
- Reduced particulate emissions. To reduce emission of particulates, better cyclones and high-efficiency electrostatic precipitators are being added to FCC units. At delayed coking units, enclosed coke conveyors and storage systems have been installed.
- Reduced CO, SO_x, and NO_x emissions. Reduction of carbon monoxide emissions requires improved efficiency in the CO boilers of FCC units. SO_x emissions from FCC units are being reduced by the hydrotreating of feedstocks, the use of SO_x-transfer additives, and the addition of flue-gas scrubbing. At some plants, limitations on NO_x may require the addition of post-combustion NO_x-removal on boilers and heaters.
- Heat-efficiency, CO₂. Energy is the largest controllable cost for a refinery. Therefore, the drive to increase heat efficiency is ever-present, especially in crude distillation units and other major energy consumers. In countries honoring the Kyoto protocol, decreased energy consumption also

decreases CO₂ emissions. Therefore, refineries in some of these countries are receiving tax credits for energy conservation projects.

- Clean water. Regulations in OECD countries require that the quality of water leaving a refinery must be at least as good as the water that enters. Tertiary treatment technology is being installed to remove lingering traces of benzene, phenols, nitrates, ammonia, and other undesirable chemicals.
- Reformulated gasoline. The need for higher octane and lower RVP in reformulated gasoline is increasing the need for alkylate and isomerate. In some catalytic reformers, severity is being reduced. Others are being converted to BTX service. More recently, MTBE units are being used for alternative purposes, such as alkylate production.
- Low-sulfur fuels. Recent rules limiting the sulfur content of gasoline and diesel fuel are stimulating hydrotreater revamps and the installation of a large number of new hydrotreaters. This in turn is requiring an increase in sulfur recovery and hydrogen-production capacity. From a process-development standpoint, the need to produce low-sulfur fuels has driven the development of new processes – SCANfining, OCTGAIN, S Zorb Prime-G, and others – for post-treating gasoline. To prevent the contamination of ultra-clean products, storage tanks and pipelines are being re-rated.

13.3 Residue Upgrading

The need for more and more heavy oil processing has been a trend since the start of the industry. Year by year the density and sulfur content of available crudes has slowly but surely been rising. Perhaps the discovery of some new oil field will change this trend, but for now, if refiners wish to continue meeting the demand for light products, they'll have to be able to process heavier feeds.

Several residue upgrading processes were mentioned in previous sections, and are described in the following chapters. The main processes are:

- Delayed coking
- Fluid-bed coking (FLEXIcoking)
- Residue hydrotreating (RDS, OCR/UFR, Resid Unionfining)
- Residue FCC (RFCC)
- Solvent deasphalting (ROSE® process)

13.4 Increased Oil Consumption in Developing Countries

The trends in *Figure 29* show that consumption of oil in OECD countries has stabilized, but consumption in the non-OECD world continues to increase. According to an article by Jeffrey Brown of FACTS Inc.,⁵⁷ China led the way

with 451,000 b/d of growth in 2003. Overall, Asia accounted for 664,000 b/d of the 1.6 million b/d of global incremental demand growth in 2003.

China will continue to drive consumption growth and affect regional product trade, prices, and refining margins. India is also likely to return to higher growth, and the region's midsize markets, such as Thailand and Indonesia, will post strong growth. In 2004, FACTS Inc. expects demand growth of 386,000 b/d in China, 22,000 b/d in South Korea, and 31,000 b/d in India. After 2004, average worldwide petroleum demand will increase by 2.5 to 3.0% per year, with Asia accounting for about half of the growth.

13.5 Automation

Advanced process control (APC) and model-predictive control (MPC) are widely used in the industry. Real-time optimization (RTO) is rather new, but its acceptance is growing Chapter 22.

APC, MPC and RTO require modern instrumentation, which includes actuator valves, distributed control systems (DCS), high-flux data highways, analyzers, and dedicated computers. They also require trained support staff, which at this writing is in short supply.

14. SUMMARY

Modern petroleum processing started in 1860. During the past 14 decades, it has grown in response to market drivers, particularly the demand for transportation fuels. In recent years, in response to economic drivers and pressure from environmental regulations, the industry has been changing.

We sincerely hope this book is a help to people who wish to gain a better understanding of the industry today.

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United States Patent [19]

Arndt et al.

[11] Patent Number: 5,198,404

[45] Date of Patent: Mar. 30, 1993

[54] PLATINUM-RHENIUM CATALYST

[75] Inventors: John H. Arndt, Berkeley; Robert L. Jacobson, Vallejo, both of Calif.

[73] Assignee: Chevron Research and Technology Company, San Francisco, Calif.

[21] Appl. No.: 786,652

[22] Filed: Nov. 1, 1991

[51] Int. Cl.⁵ B01J 21/04; B01J 23/36; B01J 27/13

[52] U.S. Cl. 502/230

[58] Field of Search 502/230, 334

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[57] ABSTRACT

A catalyst composition and process for using said catalyst is disclosed wherein the catalyst comprises 0.24 to 0.26 weight percent platinum and 0.48 to 0.52 weight percent rhenium disposed on an alumina spheroidal carrier.

3 Claims, 2 Drawing Sheets

FIG. 1

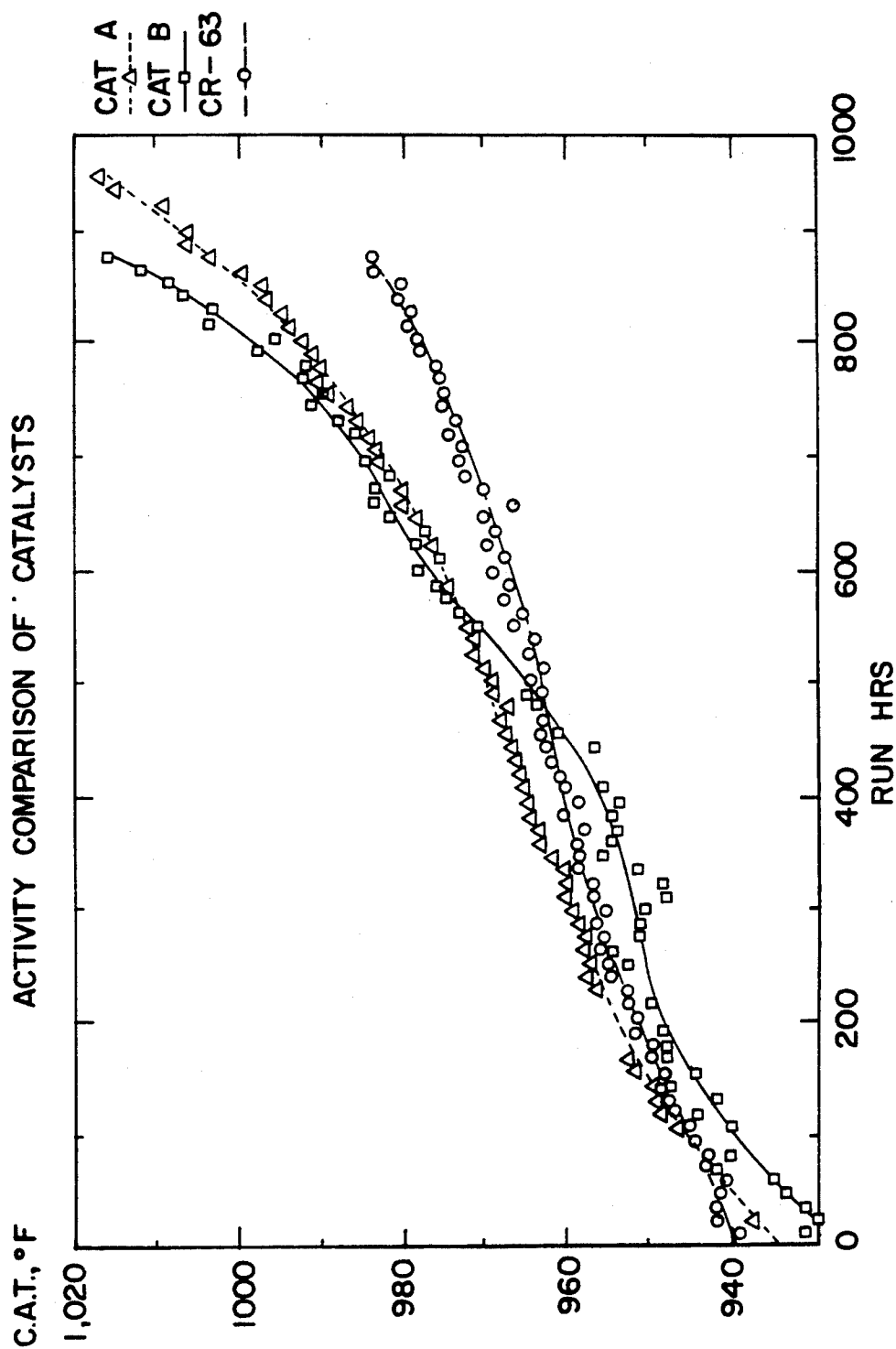
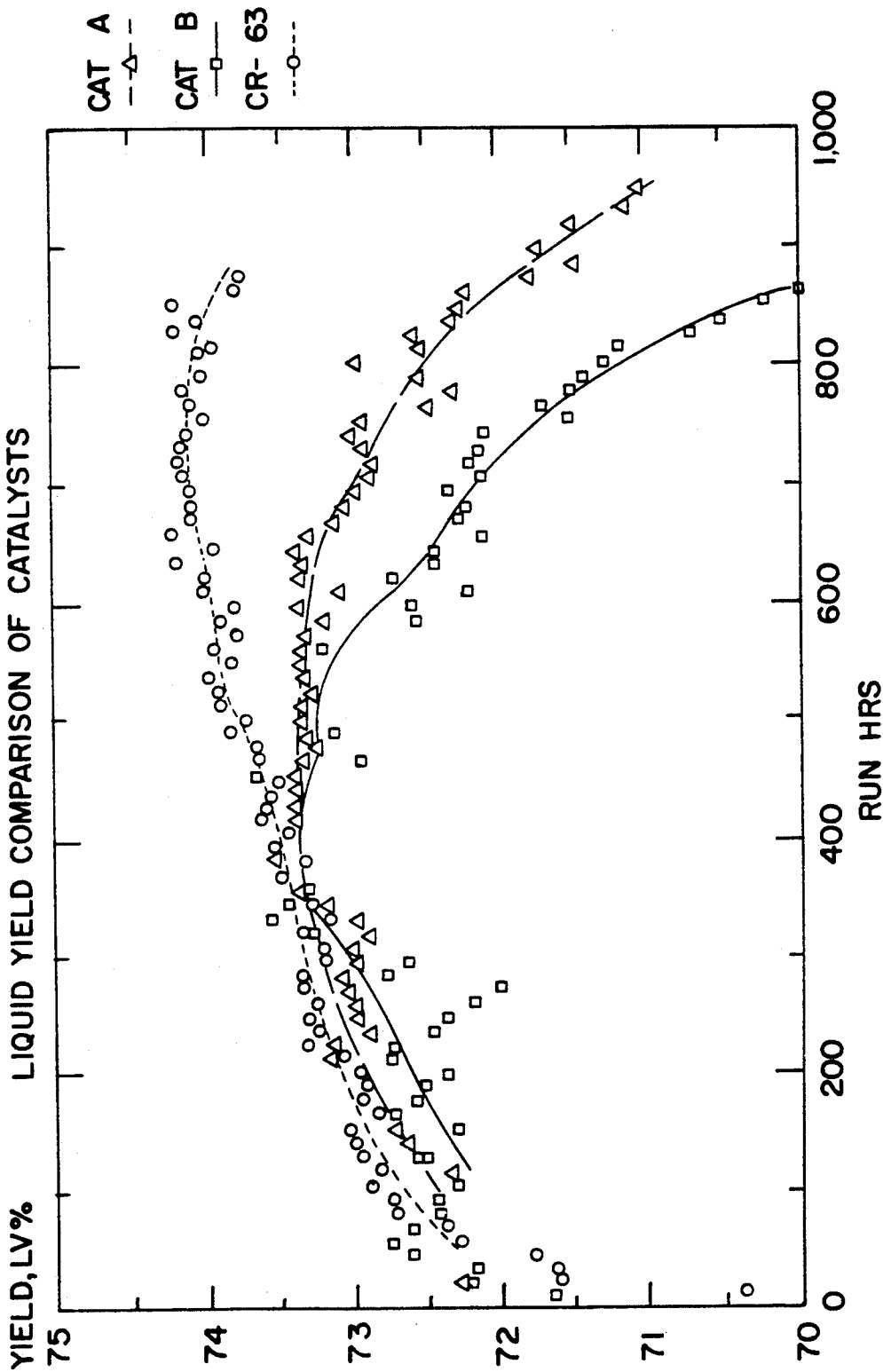


FIG. 2



PLATINUM-RHENIUM CATALYST

BACKGROUND OF THE INVENTION

This invention relates to a catalytic composite for the conversion of hydrocarbons. Additionally, the invention relates to a process for the use of the catalyst. The catalyst of the present invention is particularly useful in the catalytic reforming of hydrocarbons boiling in the gasoline range to produce in high yield a high octane reformat suitable for blending gasolines of improved anti-knock properties.

Catalytic reforming to upgrade naphtha or low-boiling range hydrocarbons to higher octane gasoline has been practiced for many years using catalysts comprising platinum on a refractory support, such as alumina. In the 1960's a major advance was made in this area when it was discovered that, in reforming a low-sulfur content hydrocarbon feedstock, the use of a catalyst comprising platinum and rhenium on alumina provided greatly improved yield stability and a much lower fouling rate. See U.S. Pat. No. 3,415,737 to Klusdahl.

Since that time, a number of other patents have issued in the area of catalytic reforming using platinum-rhenium catalysts. Some of these patents have been particularly focused on use of relatively high rhenium to platinum ratio catalysts, including the following: U.S. Pat. No. 4,356,081 to Gallagher, which discloses the use of catalysts having rhenium to platinum ratios of from about 1.08 up to as high as 17, rhenium contents from 0.362 to 0.875 weight percent and platinum contents from 0.05 to 0.344 weight percent; U.S. Pat. No. 4,425,222 to Swan, which discloses multi-stage reforming using forward reactors having a catalyst with rhenium to platinum ratio less than 1.2 a rearward reactor having a catalyst with a rhenium to platinum ratio greater than 1.5, and a swing reactor having some catalyst of each ratio.

Platinum-alumina reforming catalysts are often made by impregnating alumina with a platinum compound. For example, U.S. Pat. No. 3,617,519 discloses the preparation of a platinum-rhenium-alumina reforming catalyst wherein the platinum is impregnated into an alumina support by commingling the alumina support with an aqueous solution of chloroplatinic acid. Following the platinum impregnation, the impregnated carrier is typically dried and subjected to a conventional high temperature calcination or oxidation treatment.

U.S. Pat. No. 3,617,519 discloses that in most cases it is advantageous to adjust the concentration of the halogen component in the platinum-rhenium-alumina catalyst during the calcination step by injecting, into the air stream used therein, an aqueous solution of a suitable halogen-containing compound. U.S. Pat. No. 3,617,519 discloses that the halogen component can be added to the catalyst in various ways including adding the halogen during the impregnation through the utilization of a mixture of chloroplatinic acid and hydrogen chloride.

Typical calcination temperatures used in the preparation of the alumina support for reforming catalysts cover a wide range from about 800° to 1300° F., and frequently are 1100° F. or lower.

"Rheniforming F" catalyst, containing about 0.3 weight percent Pt, and about 0.6 weight percent Rhenium on an extruded alumina carrier has been marketed by the assignee of the present invention.

Rheniforming F has been sold under license and successfully used commercially for many years. This cata-

lyst is particularly described as the first stage catalyst of the catalyst system described in U.S. Pat. No. 4,764,267 to Chen et. al. Rheniforming F is an extruded catalyst, that is, it is substantially cylindrical in shape. The extruded Rheniforming F catalyst has a bulk density of about 0.6 cc/g and a particle density of about 1.00 cc/g. A typical tamped packed bulk density is about 0.65 cc/g.

It is typically believed the yield stability performance of Rheniforming type catalysts are due to the metals loading levels. However, in the notoriously unpredictable hydrocarbon catalysis art, a catalyst having improved yield stability and increased liquid volume yield is always much desired.

SUMMARY OF THE INVENTION

In a broad embodiment, the present invention comprises a catalyst composition comprising about 0.24 to about 0.26 weight percent platinum and about 0.48 to about 0.52 weight percent rhenium disposed on a spheroidal alumina carrier.

In an alternative embodiment, the present invention provides for a reforming process for using a catalyst composition comprising 0.24 to 0.26 weight percent platinum and 0.48 to 0.52 weight percent rhenium disposed on an spheroidal alumina carrier.

We have found catalyst performance, particularly yield stability, to be affected by sulfur content in the hydrocarbon feed to the reactor containing Pt-Re catalyst.

We believe that at reforming conditions, sulfur in the feed alters the metals/acidity balance, significantly affecting catalyst performance. The catalyst of our claimed invention performs surprisingly well in reforming of hydrocarbons, which we believe is due in part to the achievement of a metals loading which better balances the metals/acidity characteristics of the catalyst.

Among other factors, we found that when a spheroidal alumina, particularly gamma-alumina, catalyst base particles were loaded with a level of Pt and Re equivalent to the reactor-loaded density of Rheniforming F, surprisingly advantageous results were achieved in catalyst yield stability. Run-life increased about 15%, compared to the extruded Rheniforming F catalyst with the same reactor loaded metals density. Alternatively expressed, the "fouling rate" for our new catalyst was about 87% of that of Rheniforming F, with the same reactor-loaded metals density. Surprisingly, we also found LV% yield to improve for a reforming process utilizing the catalyst of the present invention. Yields of C₃'s and C₄ compounds were also lower, indicating a surprisingly lower cracking activity, and thus resulting in an increased liquid volume yield.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graphical representation of the catalytic activity over time for three catalysts: Rheniforming F, the catalyst composition of our present invention, and a third commercially available reforming catalyst.

FIG. 2 is a graphical representation of liquid yield for three catalysts: Rheniforming F, the catalyst of our present invention, and a third commercially available reforming catalyst.

DETAILED DESCRIPTION

The preferred refractory inorganic oxide for use in the present invention is alumina. Suitable alumina mate-

rials are the crystalline aluminas known as the gamma-, eta-, and theta-alumina, with gamma- or eta-alumina giving best results. The preferred refractory inorganic oxide will have an apparent bulk density of about 0.3 to about 1.01 g/cc and surface area characteristics such that the average pore diameter is about 20 to 300 Angstroms, the pore volume is about 0.1 to about 1 cc/g and the surface area is about 100 to about 500 m²/g. There are several commercial routes to pure alumina.

Although alumina is the preferred refractory inorganic oxide, a preferred alumina is that which has been characterized in U.S. Pat. Nos. 3,852,190 and 4,012,313 as a byproduct from a Ziegler higher alcohol syntheses reaction as described in Ziegler's U.S. Pat. No. 2,892,858. For purposes of simplification such an alumina will be hereinafter referred to as a "Ziegler alumina." Ziegler alumina is presently available from the Conoco Chemical Division of Continental Oil Company under the trademark Catapal. This material is an extremely high purity alpha-alumina monohydrate (boehmite) which after calcination at a high temperature has been shown to yield a high purity gamma-alumina. It is commercially available in three forms: (1) Catapal SB—a spray-dried powder having a typical surface area of about 250 m²/g; (2) Catapal MG—a rotary kiln dried alumina having a typical surface area of about 180 m²/g; and (3) Dispal, a product having a typical surface area of about 185 m²/g. For purposes of the present invention, a preferred starting material is the spray-dried powder, Catapal SB. This alpha-alumina monohydrate powder may be formed into a suitable catalyst material according to any of the techniques known to those skilled in the catalyst carrier material forming art. Spherical carrier material particles may be formed, for example, from this Ziegler alumina by: (1) converting the alpha-alumina monohydrate powder into an alumina sol by reaction with a suitable peptizing acid and water and thereafter dropping a mixture of the resulting sol and a gelling agent into an oil bath to form spherical particles of an alumina gel which are easily converted to a gamma-alumina carrier material by known methods.

Preferred carrier materials have an apparent bulk density of about 0.3 to about 0.8 g/cc and surface area characteristics such that the average pore diameter is about 20 to 300 Angstroms, the pore volume is about 0.1 to about 1 ml/g and the surface area is about 100 to about 500 m²/g. In general, best results are typically obtained with a gamma-alumina carrier material which is used in the form of spherical particles having: a relatively small diameter (i.e., typically about 1/16 inch), an apparent bulk density of about 0.75 g/cc, a pore volume of about 0.4 ml/g, and a surface area of about 175 m²/g.

The preferred alumina carrier material may be prepared in any suitable manner and may be synthetically prepared or natural occurring. Whatever type of alumina is employed it may be activated prior to use by one or more treatments including drying, calcination, steaming, etc., and it may be in a form known as activated alumina, activated alumina of commerce, porous alumina, alumina gel, etc. For example, the alumina carrier may be prepared by adding a suitable alkaline reagent, such as ammonium hydroxide, to a salt of aluminum such as aluminum chloride, aluminum nitrate, etc., in an amount to form an aluminum hydroxide gel which upon drying and calcining is converted to alumina. The alumina may be formed in any desired shape such as spheres, pills, cakes, extrudates, powders, gran-

ules, etc., and utilized in any desired size. For the purpose of the present invention, a particularly preferred form of alumina is the sphere; and alumina spheres may be continuously manufactured by the well known oil drop method which comprises: forming an alumina hydrosol by any of the techniques taught in the art and preferably by reacting aluminum metal with hydrochloric acid, combining the hydrosol with a suitable gelling agent and dropping the resultant mixture into an oil bath maintained at elevated temperatures. The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. The spheres are then continuously withdrawn from the oil bath and typically subjected to specific aging treatments in oil and an ammoniacal solution of further improve their physical characteristics. The resulting aged and gelled particles are then washed and dried at a relatively low temperature of about 300° F. to about 400° F. and subjected to a calcination procedure at a temperature of about 850° F. to about 1300° F. for a period of about 1 to about 20 hours. This treatment effects conversion of the alumina hydrogel to the corresponding crystalline gamma-alumina. Size of the spheres are determined primarily by fluid hydraulics and volume considerations in the loaded reactor. While not limiting our present invention in any way, we have found a particle size of about 1/16th inch diameter to be preferred. See U.S. Pat. No. 2,620,314, the teachings of which are fully incorporated by reference herein, for additional details. Other patents describing the oil-drop method of manufacturing spheroidal alumina carriers are U.S. Pat. Nos. 3,887,493 to Hayes, 3,919,117 to Michalko, and 3,979,334 to Lee et al., all of which are incorporated by reference herein for the teaching of the oil-drop method.

One of the advantages of a spheroidal alumina carrier is a high crush strength relative to extruded alumina carriers.

A particularly preferred alumina is that which has been produced by electrolysis. Production of alumina through electrolytic purification is well known in the art, and is described in Kirk Othmer, p. 152-154. The Encyclopedia of Chemical Processing and Design, Vol. 3, p.66-67 also describes electrolytic refining of aluminum. Electrolysis produced alumina is particularly free of impurities such as titanium compounds. While not limiting our invention in any way, or due to any particular theory of operation, we believe the absence of titanium in the alumina source gives a spheroidal catalyst, having our claimed metals loading, superior properties relative to other catalysts previously known. Additionally, electrolytically produced alumina has fewer alkali metals (such as sodium and potassium) and fewer alkaline earth metals (such as calcium and magnesium), the presence of which have been found to be undesirable in catalyst carrier material.

The platinum and rhenium are disposed in intimate admixture with each other on the porous inorganic oxide catalyst support. The platinum and rhenium can be disposed by suitable techniques such as ion-exchange, coprecipitation, impregnation, etc. One of the metals can be associated with the carrier by one procedure, for example ion-exchange, and the other metal associated with the carrier by another procedure, e.g., impregnation. However, the metals are usually associated with the porous inorganic oxide support by impregnation. The catalyst can be prepared either by coimpregnation of the metals onto the porous inorganic oxide carrier or by sequential impregnation. In general,

the carrier material is impregnated with an aqueous solution of a decomposable compound of the metal in sufficient concentration to provide the desired quantity of metal in the finished catalyst and the resulting mixture is then heated to remove volatiles. Chloroplatinic acid is an example of an acceptable source of platinum. Other feasible platinum-containing compounds, e.g., ammonium chloroplatinates and polyamineplatinum salts, can also be used. Rhenium compounds suitable for incorporation onto the carrier include, among others, perrhenic acid and ammonium perrhenates.

Incorporation of the metals with the carrier can be accomplished at various stages of the catalyst preparation. For example, if the metals are to be incorporated in intimate admixture with the alumina support, the incorporation may take place while the alumina is in the sol or gel form followed by precipitation of the alumina. Alternatively, a previously prepared alumina carrier can be impregnated with a water solution of the metal compounds. Regardless of the method of preparation of the supported platinum-rhenium catalyst it is desired that the platinum and rhenium be in intimate admixture with each other on the support and furthermore that the platinum and rhenium be uniformly dispersed throughout the porous inorganic oxide catalyst support.

The reforming activity of the catalyst is promoted by the addition of halides, particularly fluoride or chloride. Chloride is preferred. The halides provide a limited amount of acidity to the catalyst which is beneficial to most reforming operations. The catalyst promoted with halide preferably contains from 0.1 to 2 weight percent total halide content and more preferably from 0.5 to 1.5 weight percent, and still more preferably about 1 wt. % total halide content. The halides can be incorporated onto the catalyst carrier at any suitable stage of catalyst manufacture, e.g., prior to or following incorporation of the platinum and rhenium. Some halide is often incorporated onto the carrier when impregnating with the metals; e.g., impregnation with chloroplatinic acid results in chloride addition to the carrier. Additional halide can be incorporated onto the support simultaneously with incorporation of the metal(s) if so desired. In general, halides are combined with the catalyst carrier by contacting suitable compounds such as hydrogen fluoride, ammonium fluoride, hydrogen chloride, or ammonium chloride, either in the gaseous form or in a water soluble form with the carrier. Preferably, the fluoride or chloride is incorporated onto the carrier from an aqueous solution containing the halide. Preferably, low levels of halide are added during the reforming operation. This can typically be accomplished by adding an organohalide, such as *t*-butyl chloride, to the feed at a rate of about 1 ppm based upon the feed rate to the reformer.

Following incorporation of platinum and rhenium with the porous inorganic oxide, the resulting composite is usually dried by heating at an elevated temperature usually no greater than about 500° F. and preferably at about 200° F. to 400° F. Thereafter the composite is usually calcined at an even higher temperature, e.g., from about 800° F. up to about 1300° F. Calcination at less than 1100° F. is preferred.

Subsequently, the carrier containing platinum and rhenium is heated at an elevated temperature in a reducing atmosphere to convert the platinum to the metallic state and reduce the valence state of the rhenium. Preferably the heating is performed in the presence of hydrogen, and more preferably in the presence of dry hydrogen. In particular, it is preferred that this reduc-

tion be accomplished at a temperature in the range of 500° F. to 1000° F.

The catalyst composite used in the present invention, i.e., platinum and rhenium supported on a porous inorganic oxide spheroidal carrier, should be sulfided for use in the naphtha reforming process. Presulfiding can be done in situ or ex situ by passing a sulfur-containing gas, e.g., H₂S, through the catalyst bed. Other presulfiding techniques are known in the prior art. The exact form of the sulfur used in the sulfiding process is not critical. The sulfur can be introduced to the reaction zone in any convenient manner. It can be contained in the liquid hydrocarbon feed, the hydrogen rich gas, a recycle liquid stream or a recycle gas stream or any combination thereof. After operating the reforming process in the presence of sulfur for a period of time short in comparison to the over-all run length which can be obtained with the catalyst, the addition of sulfur is preferably discontinued. The purpose for presulfiding the catalyst prior to contact with the naphtha or sulfiding the catalyst during the initial contact with naphtha is to reduce excessive hydrocracking activity of the catalyst which results in the production of high yields of light hydrocarbon gases, for example, methane.

For the purposes of this invention, the end of the reforming run (EOR) is defined as the time when the liquid yield has dropped by 1 LV% from its maximum value and product octane is maintained constant or an average catalyst bed temperature of 1000° F. is reached.

The present invention will be more fully understood by reference to the following examples. They are intended to be purely exemplary and are not intended to limit the scope of the invention in any way.

EXAMPLES

Example 1

Preparation of Platinum/Rhenium Catalysts

A 2:1 rhenium to platinum spherical catalyst would be prepared by a pore-fill method by incipient wetness beginning with the following solution: a chloroplatinic acid solution which contains: 0.237 grams (g) of Pt as metal; a perrhenic acid solution which contain 0.474 g of Re as metal; and aqueous HCl which contains 1.10 g of chloride. This solution of the three components is diluted to a total volume of 59 ml with deionized water. The solution is contacted, (i.e. sprayed or slowly dripped), in a manner to assure substantially even deposition of metals on alumina. The impregnated alumina is allowed to stand for 16 hrs and then dried for 2 hrs at 250° F. Next, it is calcined for 2 hrs at 950° F. in flowing dry air. Analysis of the catalyst would show 0.24 wt % Pt, 0.48 wt % Re, and 1.0 percent Cl. The resulting catalyst has a bulk density of 0.77 g/cc, a pore volume of 0.55 cc/g, and a nitrogen surface area of 195 m²/g.

Example 2

Start-up Procedure

After the platinum and rhenium had been added to the solid support and after calcination, the catalyst was loaded in a reactor unit. The reactor was a one-inch tube with an internal diameter of $\frac{3}{4}$ inch. A volume of 80 cc of catalyst were loaded.

Dry air was passed through the reactor unit and the temperature was raised to 400° F. and held for 0.5 hour. The temperature was then raised to 600° F., held for 0.5 hour; to 800° F. and held for 0.5 hour; and to 950° F.

and held for at least 2.0 hours so that the water content of the effluent gas was 100 ppm or less. The reactor was then cooled to 800° F. with nitrogen.

The catalyst was reduced with hydrogen at 800° F., and then purged with nitrogen and cooled to 600° F. At 650° F., the feed of Example 3 was introduced at a rate of 120 cc per hour. The reactor temperature was increased to 825° F. at a rate of 25° F. per hour.

The catalyst was sulfided during feed start-up by injecting a 4.0 percent solution of di-methyl disulfide in the feed at 0.35 cc per hour. Injection continued for 5.5 hours or until sulfide break-through at about 3-5 ppm H₂S was observed. The water level was maintained below 25 ppm using a recycle dryer.

EXAMPLE 3

Feed Properties and Reforming Conditions

The feed for all the reforming runs was an Arabian Naphtha having an API gravity of 60.6; 63.5% paraffins, 27.3% naphthenes and 9.2% aromatics. The D-86 distillation (%—° F.) showed start—168; 5—202; 10—210; 20—218; 30—226; 40—234; 50—241; 60—253; 70—269; 80—289; 90—316; 95—331 end—377.

Reaction conditions were 200 psig, 2.0 liquid hourly space velocity (LHSV), 3.5 hydrogen to fresh feed hydrocarbon mol ratio, and constant product octane of 100 RON. T-butyl chloride was injected (1 ppm) with the feed to maintain the chloride level on the catalyst at about 1 wt. %.

Example 4

Comparative Catalyst A

A 1:2 Pt/Re catalyst was prepared as in Examples 1 and 2, except that the catalyst base was an alumina extrudate, substantially cylindrical in shape, having the following properties: Surface Area was equal to about 190 M²/G, particle density was equal to about 0.98

measured on base before impregnation, Chloride wt. % was equal to about 1.4%. Metal loadings were 0.3 wt % Pt and 0.6 wt % Re.

Example 5

Comparative Catalyst B

A commercially available extruded and substantially cylindrical reforming catalyst, CAT B, having a metals loading of 0.22 wt % Pt and 0.44 wt % Re was purchased from a commercial catalyst supplier. The startup procedure of Example 2 was used.

Example 6

Reforming Comparisons

The three catalysts—the catalyst of this invention prepared by Examples 1 and 2, the catalyst of Example 4 and the Catalyst of Example 5 were compared at substantially identical reaction conditions with identical feeds, as described in Example 3. Metal loadings in the reactor were substantially identical at 0.12 lbs/ft³ Pt, and 0.24 lbs/ft³ Re for the catalyst of our invention and comparative catalyst A.

The results are shown in FIGS. 1 and 2. As can be seen, the catalyst of the present invention, labelled "CR-63", gives improved life (defined by end-of-run at 1000° F.) and improved liquid volume yields.

What is claimed is:

1. A catalyst composition comprising 0.5 to 2.0 weight percent chlorine, 0.24 to 0.26 weight percent platinum and 0.48 and 0.52 weight percent rhenium disposed on a spheroidal alumina carrier.

2. The catalyst composition of claim 1 wherein the alumina is gamma-alumina.

3. The catalyst composition of claim 1 further comprising about 1 weight percent chlorine.

* * * * *



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RESEARCH ARTICLE

Synthetic zeolites and other microporous oxide molecular sieves

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This article has a Correction. Please see:

- May 23, 2000

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Abstract

Use of synthetic zeolites and other microporous oxides since 1950 has improved insulated windows, automobile air-conditioning, refrigerators, air brakes on trucks, laundry detergents, etc. Their large internal pore volumes, molecular-size pores, regularity of crystal structures, and the diverse framework chemical compositions allow “tailoring” of structure and properties. Thus, highly active and selective catalysts as well as adsorbents and ion exchangers with high capacity and selectivity were developed. In the petroleum refining and petrochemical industries, zeolites have been made possible cheaper

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and lead-free gasoline, higher performance and lower-cost synthetic fibers and plastics, and many improvements in process efficiency and quality and in performance. Zeolites also help protect the environment by improving energy efficiency, reducing automobile exhaust and other emissions, cleaning up hazardous wastes (including the Three Mile Island nuclear power plant and other radioactive wastes), and, as specially tailored desiccants, facilitating the substitution of new refrigerants for the ozone-depleting chlorofluorocarbons banned by the Montreal Protocol.

Relationships of Synthetic Zeolites to Natural Zeolites and Other Minerals.

Only 6 of the >63 natural zeolites commonly occur in large beds: analcime (ANA),* chabazite (CHA), clinoptilolite (HEU), erionite (ERI), mordenite (MOR), and phillipsite (PHI) (1); ferrierite (FER) occurs in a few large beds. Each of the seven also has been synthesized, but only mordenite and ferrierite are manufactured in large quantity. Significantly, synthetic mordenite has large pores whereas natural mordenite has small pores (2).

Besides mordenite and ferrierite, the principal synthetic (aluminosilicate) zeolites in commercial use are Linde Type A (LTA), Linde Types X and Y (Al-rich and Si-rich FAU), Silicalite-1 and ZSM-5 (MFI), and Linde Type B (zeolite P) (GIS). Other commercially available synthetic zeolites include Beta (BEA), Linde Type F (EDI), Linde Type L (LTL), Linde Type W (MER), and SSZ-32 (MTT). All are aluminosilicates or pure silica analogs.

Recently, new nonaluminosilicate, synthetic molecular sieves became available commercially. They include aluminophosphates (family of AlPO_4 structures); silicoaluminophosphates (SAPO family); various metal-substituted aluminophosphates [MeAPO family, such as CoAPO-50 (AFY)]; and other microporous framework structures, such as crystalline silicotitanates.†

Most current commercial applications use aluminosilicate zeolites or their modified forms. Undoubtedly, commercial uses both for zeolites and other molecular sieves will continue to grow.

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Development of Synthetic Zeolites and Other Microporous Oxides.

The first zeolite mineral (stilbite) was described in Sweden by Baron Cronstedt in 1756 (3–5). Highlights of the history of adsorption studies of zeolites were reviewed by Breck (6).

By 1926, the adsorption characteristics of chabazite were attributed to tiny pores (<5 Å in diameter) that allowed small molecules to enter but excluded larger ones: hence, the term “molecular sieve” (7).

By 1945, Barrer classified zeolite minerals into three classes depending on the size of the molecules adsorbable rapidly, slowly, or not appreciably at room temperature (8). However, zeolites did not find any significant commercial use until synthetic zeolites were discovered and developed (large, **Continue** Find out more)

mineable deposits of natural zeolites were not discovered until the late 1950s). Barrer's 1948 synthesis of small-pore mordenite at high temperatures and pressures heralded the era of synthetic zeolites (**10**).

From 1949 through the early 1950s, the commercially significant zeolites A, X, and Y were discovered by Milton and Breck at the Tonawanda, New York, laboratories of the Linde Air Products Division of Union Carbide Corporation. These zeolites were synthesized from readily available raw materials at much lower temperature and pressure than used earlier. Many of the new synthetic zeolites had larger pore size than most of the known natural zeolites, allowing applications involving larger molecules. In addition, many had larger pore volume, giving higher capacity.

In 1953, Linde Type A zeolite became the first synthetic zeolite to be commercialized as an adsorbent to remove oxygen impurity from argon at a Union Carbide plant (**11**). Synthetic zeolites were introduced by Union Carbide as a new class of industrial adsorbents in 1954 and as hydrocarbon-conversion catalysts in 1959. New zeolites and new uses appeared steadily through the 1960s. An explosion of new molecular sieve structures and compositions occurred in the 1980s and 1990s from the aluminosilicate zeolites to the microporous silica polymorphs to the microporous aluminophosphate-based polymorphs and metallo-silicate compositions (**12**). Molecular sieves now serve the petroleum refining, petrochemical, and chemical process industries as selective catalysts, adsorbents, and ion exchangers.

Many zeolites can be synthesized with SiO_2 higher or lower than in nature for the same framework type. Higher SiO_2 generally gives greater hydrothermal stability, stronger-acid catalytic activity, and greater hydrophobicity as adsorbents. Conversely, lower SiO_2 gives greater cation exchange capacity and higher adsorbance for polar molecules. Controlling the synthesis process optimizes a zeolite for different applications.

Many synthetic zeolites have framework topologies not found to date among the natural zeolites. The natural zeolite faujasite has the same framework (FAU) and similar framework composition to the Type Y synthetic zeolite but is rare in nature.

Where both natural and synthetic forms of the same zeolite are available in commercial quantity, the variable phase purity of the natural zeolite and the chemical impurities, which are costly to remove, can make the synthetic zeolite more attractive for specific applications. Conversely, where uniformity and purity are not important, the cheapness of a natural zeolite may favor its use. Hence, natural and synthetic zeolites seldom compete for the same applications.

Structure and Properties of Synthetic Molecular Sieves.

Zeolites have the chemical formula $\text{M}_{2/n}\text{OAl}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where the charge-balancing nonframework cation M has valence n , x is 2.0 or more, and y is the moles of water tetrahedral atoms, or T-atoms, form a three-dimensional (3D) frame

The Al and Si
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linked together by shared oxygen ions. Although an SiO_4 tetrahedra is charge-balanced, an AlO_4 tetrahedra has a negative charge balanced by a positive charge on M . Related pure SiO_2 frameworks, such as silicalite-1 (MFI), are charge-balanced and do not need nonframework cations.

Variants involve Ge substitution for Si in the framework or involve substitution of Fe, Co, Mn, Zn, Ti, or Mg for Al. In the related aluminophosphates (AlPO_4), each negatively charged AlO_4 tetrahedron is balanced by a positively charged PO_4 tetrahedron, and nonframework cations are not needed. Still other variants include the silicoaluminophosphate (SAPO) structures in which Si substitutes some P in the AlPO_4 framework; each added Si needs a nonframework cation to balance the charge on the framework.

The pore geometry and volume in a specific microporous oxide are determined by the specific topology of the particular 3D framework. The lower the T-atom density per volume of the zeolite crystal, the higher the void fraction inside the crystal. The void fraction is 50% for NaX and 47% for NaA. The size of the largest pore in a zeolite is determined by the number of oxygen ions rimming the pore and its shape; e.g. a planar, circular eight-ring (8R) pore rimmed by eight oxygen ions has a diameter of 4.1 Å, as in Linde Type A zeolite, whereas the elliptical 8R pore of NaP zeolite (GIS) is 4.5×3.1 Å.

Applications in separation and purification processes often used the ability of zeolites and other molecular sieves to exclude molecules too large to enter the pores and admit smaller ones. Similarly, shape-selective catalysis takes advantage of the ability of the pores to favor the admission of smaller reactant molecules, the release of smaller reaction product molecules, or the restriction of the size of transition-state complexes inside the micropores of the zeolite (13).

Petroleum Refining Processes for the Production of Fuels

Catalytic Cracking.

The prime goal in petroleum refining is efficient conversion of crude oil into high-quality fuel components. Desired fuel fractions in order of increasing molecular weight are gasoline, aviation jet fuel, and diesel fuel. Gasoil and asphalt, with even higher molecular weight, are most often further processed by thermal cracking, catalytic cracking (to make gasoline) (14), and catalytic hydrocracking (to make jet fuel). A lower-boiling fraction, light straight-run naphtha, rich in pentanes and hexanes and some butane, is further processed by catalytic hydroisomerization.

Strong acid catalytic activity of X and Y zeolites was discovered in 1957 by Rabo and was related to their crystallinity (15). This discovery laid the basis for zeolites in cracking, hydrocracking, and isomerization of hydrocarbons. From the early 1960s on, use of synthetic zeolites in catalysis and in related adsorption separation processes has dramatically transformed petroleum refining by vastly increasing the yield of high-quality fuels and reducing capital and operating costs, energy requirements, and adverse environmental impact. Zeolites also played a major role in allowing formulation of gasoline to the present lead-free gasoline.

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In modern petroleum refineries in the world, gasoil and other heavier fractions from the crude oil fractionation unit are fed to fluid catalytic cracking units, which use small, fluidizable catalyst particles containing Type Y zeolite or other zeolites, or to hydrocracking units, which use fixed beds of larger catalyst particles also containing zeolites. The fluid catalytic cracking and hydrocracking units convert higher-molecular-weight hydrocarbons to lighter ones suitable for gasoline, light fuel oils, olefins, and other uses.

In both fluid catalytic cracking and hydrocracking, zeolite catalysts provide vastly superior combinations of strong acid catalytic sites, uniformity of pore structure, and stability, all of which provide improved selectivity, yield, durability, and cost over nonzeolite alternatives. In addition, these zeolites have provided much higher yield of gasoline and other high-quality fuels per barrel of crude oil, significantly reducing crude oil imports to the U.S. (>400 million barrels a year) and to other countries.

Hydrocracking.

The early 1960s saw increasing demand for high-octane gasoline for the high-compression-ratio engines in new high-performance cars. Demand also grew for diesel fuel for diesel-electric locomotives and low-freeze-point jet fuel. These needs were met by rapid growth in hydrocracking of the more-refractory crude fractions that were not converted to gasoline and lighter products in the catalytic cracking units. This growth was accompanied by the pioneering development by Roland Hanford at Union Oil, now Unocal, of new, zeolite-based hydrocracking catalysts with dramatically improved activity and selectivity. Hydrocracking grew rapidly in the 1960s and 1970s inside and then later outside the U.S. Worldwide hydrocracking capacity should grow from ≈ 2.5 million barrels per day in 1990 to ≈ 3.5 million in 2000 (16).

In hydrocracking, hydrocarbon molecules and hydrogen gas pass over the zeolite catalyst, which converts higher-molecular-weight petroleum fractions to lower-molecular-weight fuels (17). For example, UOP's Unicracking process (developed jointly by the Molecular Sieve Department of Union Carbide, now part of UOP, and Unocal) uses base- or noble-metal hydrogenation-activity promoters impregnated on combinations of zeolite- and amorphous-aluminosilicates for cracking activity (18). The specific metals chosen and the proportions of the metals, zeolite, and nonzeolite aluminosilicates are optimized for the feedstock and desired product balance. The Isocracking process of Chevron also uses hydrocracking catalysts, some containing zeolites to increase the cracking function of these dual-function catalysts (19).

The zeolites most frequently used in commercial hydrocracking catalysts are partially dealuminated and low-sodium, or high-silica, Type Y zeolites in hydrogen or rare-earth forms. Other zeolites and mixtures of zeolites also are used. The zeolites often are imbedded in a high-surface-area amorphous matrix, which serves as a binder. The metals can reside inside the zeolite and on the amorphous matrix.

Catalytic Dewaxing.

Catalytic dewaxing yields various grades of lube oils and fuel components suitable for extreme winter conditions. Paraffinic (waxy) components, which precipitate out at low temperatures, are removed. In the UOP Catalytic Dewaxing process, the first stage saturates olefins and denitrifies the

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feed via hydrotreating (20). In the second stage, a dual-function, non-noble-metal zeolite catalyst selectively adsorbs and then selectively hydrocracks the normal and near-normal long-chain paraffins to form shorter-chain (nonwaxy) molecules. Alternatively, as in the recently commercialized Chevron Isodewaxing process, the dewaxing results from isomerizing the linear paraffins to branched paraffins by using a SAPO-11 molecular sieve catalyst containing platinum (21, 22).

Light Paraffin Hydroisomerization.

Lead was added to gasoline to increase its octane number, especially for vehicles, introduced in the early 1960s, that had modern high-compression-ratio, high-performance engines. The subsequent U.S.-legislated reduction of lead in gasoline required increased use of the catalytic hydroisomerization of the light straight-run naphtha fraction mentioned earlier.

Some versions of UOP's hydroisomerization processes use highly active zeolite-based, Pt-containing hydroisomerization catalysts, such as UOP I-7, which contains modified synthetic (large-pore) mordenite. In the presence of hydrogen at moderate conditions, such catalysts optimize isomerization and minimize hydrocracking (23). Linear paraffins in the feed convert to branched paraffins with higher octane number. The Sud-Chemie HYSOPAR catalyst used in CEPSA's CKS ISOM process also uses a zeolite for the hydroisomerization of light naphtha.‡

To further increase octane level, products from a hydroisomerization unit can be sent to the Molex process, where the remaining lower-octane, linear paraffins are separated from the other compounds by using a zeolite adsorbent and a liquid desorbent; the Molex process is an example of UOP's Sorbex simulated-moving-bed technology (24). The extracted linear paraffins are recycled to the hydroisomerization unit, and the remaining higher-octane fraction is recovered for gasoline blending. The combination of the hydroisomerization and Molex processes boosts the research octane number of a typical feed from 68–70 to 89–92.

Alternatively, if a refinery can use the linear paraffins, it need not recycle them to a hydroisomerization unit. For example, the paraffins may be added to the feed of an ethylene steam cracker, thus increasing the efficiency of the cracker and leading to lower energy consumption and a purer product. Linear paraffins also are used as intermediaries in some food processing.

UOP's once-through zeolitic isomerization process (formerly known as the Shell Hysomer process) also uses a strongly acidic zeolite with a noble metal to hydroisomerize the light naphtha (25). Refiners with idle catalytic reformers or hydrotreaters can convert this equipment to use this process. To achieve higher octane levels, UOP's TIP total isomerization process uses the once-through isomerization process combined with UOP's IsoSiv process, which uses size-selective zeolite adsorption of the unreacted linear paraffins so that they can be recycled and converted to extinction (32). Both the TIP and IsoSiv processes originally were developed at Union Carbide's Molecular Sieve Department, now part of UOP.

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Petrochemicals Processing for Aromatics Production and Derivatives

Ethylbenzene Synthesis.

Styrene monomer, made by dehydrogenating ethylbenzene (EB), is the basic chemical for all polystyrene products. Ethylbenzene is made by using various catalysts to alkylate benzene with ethylene. Until 1980, nearly all EB was produced by liquid-phase alkylation reactions using aluminum chloride catalyst. In 1980, vapor-phase alkylation using a heterogeneous catalyst was introduced to eliminate many problems of waste disposal and special metallurgy involving aluminum chloride. In 1990, liquid-phase zeolitic technology began to replace the Mobil/Badger vapor-phase process, based on ZSM-5 zeolite.

The 1990 Lummus/UOP ethylbenzene liquid-phase process, using highly stable, poison-resistant zeolite catalysts manufactured by UOP, operates at low benzene-to-olefin ratio and high selectivity to EB. § The UOC-4120 catalyst from UOP, used initially for both alkylation of benzene with ethylene and transalkylation of polyethylbenzenes and benzene to produce more EB, operated successfully for 7 years, with >5 million metric tons of capacity installed or ordered. The extremely low xylene content of the EB product permits the production of the highest-purity styrene monomer and lowers the costs in the styrene production unit. Current designs use the EBZ-100 catalyst for transalkylation and the EBZ-500 catalyst for alkylation. The new Mobil/Badger-Raytheon EBMax process commercialized in 1995 uses an MCM-22 (MWW) zeolite catalyst for liquid-phase alkylation; Mobil's TRANS-1 modified MFI catalyst for vapor-phase transalkylation of polyethylbenzene and cracking of C₆ and C₇ naphthenes; and TRANS-4 catalyst for liquid-phase transalkylation of polyethylbenzenes (26).

Cumene Synthesis.

More than 95% of the 7 million metric tons per year of cumene is used worldwide as the principal chemical for production of phenol and its acetone byproduct. The phenol yields phenolic resins, bisphenol-A, caprolactam, and other products. Phenolic resins are used extensively to bond plywood and composition board. Both phenol and acetone are used increasingly in the production of polymers such as epoxy, polycarbonate resins, and nylon-6.

Most cumene is made by alkylating benzene with propylene over an acid catalyst, mostly solid phosphoric acid and minor AlCl₃. Recent awareness of the negative environmental impact of spent-catalyst disposal has spurred a search for more benign alternatives. The world's leading technology (90% open market) for producing cumene is the UOP Catalytic Condensation process, which uses inexpensive solid phosphoric acid catalyst. Its high-purity cumene product has set the standard. However, side reactions over the solid phosphoric acid catalyst result in a 4–5% loss in cumene yield.

The UOP Q-Max process, commercialized in 1996, uses the new, environmentally benign QZ-2000 zeolite catalyst for direct alkylation of benzene with propylene and incorporates a second step (transalkylation) to react the diisopropylbenzene, a byproduct of the

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additional cumene.[¶] It produces a higher-quality cumene product (>99.97% purity) at overall cumene yield of 99.7% and lower investment cost.

The Mobil-Badger process using aluminum chloride catalyst also yields cumene. Recently, Mobil/Raytheon also developed a zeolite catalyst based on the relatively new zeolite MCM-22. Similarly, Dow and Kellogg developed “3D-DM” catalysts based on dealuminated forms of mordenite (27); Enichem, a catalyst based on zeolite Beta, and CD-Tech/Lummus, a catalytic distillation zeolite catalyst.

para-Xylene Production from Mixed C₈ Aromatics.

Polyester fibers have revolutionized clothing. Many people in the U.S. take for granted wash-and-wear and permanent press clothing, and ironing of shirts is out of fashion. Demand has grown in developing countries because of the great comfort of fabrics made from cotton–polyester fibers blended in any proportion for any climate, as well as low cost, excellent durability, and ease of washing with little water and detergent (M. M. Sharma, personal communication).

The worldwide annual production of 12–15 million tons *p*-xylene is expected to rise to ≈17–18 million tons in 10 years. Most *p*-xylene is used to make purified terephthalic acid, which is reacted with ethylene glycol to make the poly-(ethylene terephthalate), the basis of polyester fibers. The *p*-xylene is separated from mixed C₈ aromatics (containing *o*-, *m*-, and *p*-xylenes and EB) by using either crystallization or adsorption processes. Since 1971, the new UOP's Parex adsorption separation process captured 60% of the worldwide *p*-xylene production. Another large and growing use for *p*-xylene is in the manufacture of poly-(ethylene terephthalate) for bottles recyclable and environmentally benign.

The Parex process uses the Sorbex technology mentioned earlier (28). Its critical ingredient is a special, *p*-xylene-selective adsorbent. Ion-exchanged forms of synthetic FAU zeolite are used with desorbent liquids to recover >97% *p*-xylene at >99.9% purity from a raffinate containing EB and *o*- and *m*-xylenes.

Xylene Isomerization.

The raffinate from the Parex unit can go to an Isomar unit (29), licensed by UOP, for isomerization to a near-equilibrium mixture of xylenes, which are recycled to the Parex unit. The Isomar unit itself also uses UOP zeolite acid catalysts, such as the Pt-bearing I-9 catalyst, which converts EB to xylenes, and the I-100 catalyst, which dealkylates EB to benzene. Both provide efficient EB conversion with excellent xylene retention.

Disproportionation of Toluene and Transalkylation of Toluene and Trimethylbenzenes.

Recent strong demand for *p*-xylene has begun to exceed the supply of mixed xylenes. Incorporating the Tatoray process (originated with Toray Industries in Japan and further developed and licensed by UOP) into the aromatics complex in a refinery can more than double the yield of *p*-xylene from a naphtha feedstock (30). The zeolite-based TA-4 catalyst has two principal functions, disproportionation of toluene into the more-valuable benzene and mixed xylenes, and transalkylation of toluene and trimethylbenzenes to mixed xylenes. The mixed xylenes then are added to the Parex unit to produce more *p*-xylene.

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***p*-Xylene Synthesis from Toluene.**

Xylenes can be produced by the zeolite-catalyzed disproportionation of toluene alone. Mobil developed the MTPX (Mobil toluene to *para*-xylene) process for internal use, and the licensed MSTDP (Mobil selective toluene disproportionation) process, based on ZSM-5 (MFI) “product shape-selective” zeolite catalysts (31). The toluene disproportionation generates mixed xylenes inside the catalyst, but the overall relative yield of *p*-xylene is greater than the thermodynamic equilibrium allows because the *p*-xylene diffuses more rapidly out of the zeolite than do the *o*- and *m*-xylenes. UOP’s recent PX-Plus process also uses a zeolite catalyst for *p*-xylene synthesis by shape-selective disproportionation of toluene.

Aromatics from Light Hydrocarbons.

UOP’s Cyclar process converts low-value LPG (propane, butanes) or light feedstocks containing olefins and paraffins to high-value, easily transportable, petrochemical-grade liquid aromatic products, particularly BTX (benzene, toluene, and xylenes). It uses a single gallium-modified zeolite catalyst developed by BP and UOP in conjunction with UOP’s CCR continuous catalytic regeneration system (32, 33). Acidic sites on the zeolite catalyze dehydrogenation, oligomerization, and cyclization. The shape-selectivity of the zeolite cavities helps promote the cyclization reactions and limits the size of the rings (34).

M-Forming.

Catalytic reforming produces a high-octane liquid reformate product rich in aromatics and hydrogen gas; light hydrocarbon gases, such as LPG; and C₆ to C₉ paraffins. Mobil’s M-Forming process selectively hydrocracks linear and singly branched paraffins in gasoline reformate fractions to LPG by size-selective catalysis by using medium-pore ZSM-5 zeolite (35). Olefins produced from paraffin cracking alkylate the aromatics and also form some aromatics by oligomerization.

Other Aromatics Produced by Sorbex Separations.

Some other applications of the Sorbex zeolite-based simulated-moving-bed technology (36) are MX the Sorbex process, *m*-xylene from EB and *o*- and *p*-xylenes; the Cymex process, *m*- and/or *p*-xylene from a mixture of cymene isomers; and the Cresex process, *m*- and/or *p*-cresol from mixtures of cresol and xylenol.

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Petrochemicals Processing for Olefins Production

Light Olefin Production by Methanol-to-Olefins (MTO) Process.

Only ≈110 of the ≈2,500 billion cubic meters of natural gas produced annually is wasted (burned in flares). About 103 billion cubic meters per year of natural gas are processed to make liquefied natural gas, but at high cost. Alternatively, natural gas can be converted first to syngas (CO and H₂) and then to the more-valuable, easily shipped methanol. However, the methanol market is too small for the available natural gas.

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The new UOP/HYDRO MTO process provides the means to efficiently convert methanol to even more valuable light olefins (ethylene, propylene, and butenes), which have large, commodity-type petrochemical markets: Ethylene and propylene represent the largest, together accounting for 120 million MTA, and growing (37). This process uses the product-shape-selective UOP MTO-100 catalyst based on a unique molecular sieve. During the late 1980s, Norsk Hydro, assisted by Sintef, started independent work, and UOP and Hydro agreed on joint development of the process, now available from UOP for commercial licensing. Norsk Hydro is running a large (0.75 metric tons/day) UOP/HYDRO MTO demonstration plant in Porsgrunn, Norway.

Olefin Isomerization.

The 1990 Clean Air Act increased the demand for blendable ethers in motor fuels and created a demand for isobutene to make methyl tertiary butyl ether and for isopentene to make tertiary amyl methyl ether. In anticipation, the UOP I-500 catalyst, based on a SAPO structure, and two new processes were developed: Butesom for isobutene isomerization and Pentosom for pentene isomerization (38–41). In both processes, coke progressively accumulates on the catalyst and is periodically removed by a simple carbon burn-off in the reactor. The Lyondell IsoPlus process (42, 43) uses a ferrierite (FER) zeolite for the isomerization of olefins to isoolefins, and a Mobil patent (44) describes using a medium-pore zeolite catalyst (for example, ZSM-5) for similar applications.

Oxygenates Removal Unit.

Zeolite adsorbents are used in a UOP oxygenate removal unit down to >1 ppm total of trace oxygenates (e.g., DME, methanol, and methyl tertiary butyl ether) from C₄ streams. Depending on the flow scheme, the C₄ stream generally goes to a motor fuel alkylation (sulfuric acid or hydrofluoric acid) process or is recycled to a dehydrogenation-etherification complex, which has a UOP Oleflex unit and a methyl tertiary butyl ether unit. The advantages of the oxygenate removal unit is that it minimizes the acid consumption otherwise associated with these oxygenates, thus minimizing the acid neutralization wastes, a significant environmental benefit (B. V. Vora, personal communication). In dehydrogenation, the oxygenate removal unit improves catalyst stability and lowers costs of methyl tertiary butyl ether production.

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Petrochemicals Processing for Detergents Production

Linear Paraffins for Biodegradable Detergents.

Petroleum derivatives account for most of the total surfactant production and household detergents. During the 1940s and 1950s, sodium dodecylbenzene sulfonate was the most widely used synthetic detergent. However, the dodecyl paraffin side group on the benzene ring is highly branched and not easily biodegraded. In the early 1960s, environmental concerns led to development of linear alkylbenzene sulfonate (LAS) detergents, which are both biodegradable and cost-effective.

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The key to the manufacture of the linear paraffins required to make linear alkylbenzene (LAB) and, hence, LAS is the use of size-selective synthetic zeolites that adsorb linear paraffins but exclude branched paraffins, naphthenes, and aromatics from mixtures spanning a range of boiling points, as in kerosene (C_{12} to C_{18}). Although anticipated by the work of McBain (7) and Barrer (8–10), such a class separation of molecules spanning a range of boiling points was virtually impossible before development of the synthetic molecular sieves by Union Carbide in the 1950s. Two different processes, one vapor phase and the other liquid phase, are used.

The vapor-phase IsoSiv process was developed at Union Carbide originally for octane improvement. To produce linear paraffins for detergents, kerosene feed, pretreated to acceptable quality and the desired carbon number range, passes at elevated temperature and just over atmospheric pressure through a bed of zeolite adsorbent that adsorbs just the linear paraffins. Just enough hexane vapor follows the kerosene feed to displace the nonadsorbed feed and isomeric hydrocarbons from the void spaces in the adsorber vessel. The effluent from this step is combined with the adsorption effluent stream. The linear paraffins adsorbed in the zeolite are desorbed by purging the bed in the opposite direction with hexane. The hexane in the effluent is separated by distillation and is recycled. The remaining linear paraffins comprise the desired product.

The liquid-phase Molex process, mentioned earlier, is most often used to produce plasticizers (C_6 – C_{10}), LABs (C_{10} – C_{15}), and detergent alcohols (C_{13} – $C_{22}+$, but usually heavier than C_{16}). To make linear paraffins for LAB, increased linearity and low aromatics content are desired. The new high-purity Molex process has improved product purity to 99.7% and reduced aromatics content to 0.05 wt %. In addition, the new OP ADS-34 zeolite adsorbent provides improved long-term separation performance in the Molex process.

The linear paraffins made in the Molex process can be sent to UOP's Pacol and DeFine processes (45) for catalytic conversion to monoolefins. These pass to a UOP Detergent Alkylate process (46), which uses a hydrofluoric acid catalyst, or to a Detal process (offered for license in 1995II), which uses a more environmentally friendly solid, heterogeneous catalyst to produce LAB from the monoolefins plus benzene. Unreacted linear paraffins are recycled to the Pacol and DeFine units and are converted to extinction. These catalytic processes use nonzeolite catalysts.

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Linear Olefins for Detergent Alcohols.

As discussed previously, LAB accounts for half of the detergent intermediate market. Detergent alcohols made from linear olefins are another quarter. Detergent alcohols are made from C_{10} – C_{15} alpha olefins derived from ethylene or from C_{10} – C_{15} internal olefins derived from lower-cost kerosene feed.

Linear olefins of improved purity are increasingly sought. Linear paraffins from the new high-purity Molex zeolite adsorption process are sent to the Pacol and DeFine processes to convert them to a mixture of monoolefins plus unreacted linear paraffins. The mixture is fed to UOP's Detergent Alkylate process, which uses a hydrofluoric acid catalyst, or to a Detal process, which uses a more environmentally friendly solid, heterogeneous catalyst to produce LAB from the monoolefins plus benzene. Unreacted linear paraffins are recycled to the Pacol and DeFine units and are converted to extinction. These catalytic processes use nonzeolite catalysts.

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unreacted paraffins, which are recycled back to the Pacol and DeFine units to extinction. The Olex process now uses the new UOP ADS-32 zeolite adsorbent, which provides improved capacity and rates. The linear olefins product has improved product purity (reduced aromatics and diolefins) as a result of improvements in the zeolite adsorbents and in the nonzeolite catalysts and operating conditions in the Molex-Pacol-DeFine-Olex sequence of processes.

Separation and Purification Process Applications

Molecular sieve adsorbents are used in many other separation and purification applications: (i) petroleum refining processes, used to remove CO₂, chlorides and mercury from a variety of streams; to dry and purify liquids and gases in diverse applications; to treat alkylation unit feed to reduce acid consumption, regenerator use, and corrosion, and to treat refinery hydrogen to prevent corrosion in downstream equipment; to dry and desulfurize refined products; and to dry and purify feed and recycle hydrogen in isomerization units; (ii) petrochemicals, used to dry hydrocarbon liquids, cracked gas, and hydrogen; to dry and purify natural gas liquids, ethane and propane feedstocks in ethylene and polymer plants; and in ethylene, propylene, butadiene, butylenes, amylenes, and various other comonomers and solvents; (iii) natural gas treating, used to dry and desulfurize natural gas to protect transmission pipelines and to remove undesirable impurities from home cooking and heating gas and to desulfurize ethane, propane, and butane and for H₂O and CO₂ removal before cryogenic processing; (iv) industrial gas production and purification, used to remove H₂O and CO₂ from air before liquefaction and separation by cryogenic distillation, for pressure swing adsorption (PSA) separation of air, and in PSA purification of hydrogen by using zeolites and other adsorbents, such as activated carbon; (v) specialty and fine chemicals and pharmaceuticals, used for drying; for removal of impurities, including odors; and for other applications in the manufacture of specialty and fine chemicals and pharmaceuticals. Common features of these uses are now summarized.

Preprocessing of Gases before Cryogenic Separations.

Deep drying and CO₂ removal are required before cryogenic liquefaction and subsequent separation processing to prevent formation of ice and dry ice, which would plug up the cryogenic processing equipment. Several synthetic zeolites exhibit great affinity for polar compounds such as H₂O and CO₂ and have high adsorption capacity at ambient temperature. They are used extensively in processing natural gas to make liquefied natural gas or to recover hydrocarbon liquids or helium; in processing air to make O₂, N₂, and Ar in cryogenic air-separation plants; and in treating ethylene and other olefins formed in ethylene steam-cracking plants before separation in cryogenic distillation separation units. These pretreatments work to perfection: Passing ambient air over such zeolite adsorbents at room temperature makes the air drier (−60°C dew point or lower) than in the coldest part of Alaska in the depth of winter.

Because the adsorbed impurities are strongly held on the zeolite adsorbents, they are regenerated for subsequent reuse in thermal-swing processes that pass a hot regenerative gas over the spent zeolite to heat it and to carry away the adsorbed compounds. The zeolite then returns to ambient temperature

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and is used to treat more gas.

Removal of Impurities from Gases and Liquids Down to Low Levels.

Because zeolites bind strongly to polar compounds, including hydrogen sulfide, mercaptans, organic chlorides, CO, and to mercury, they can purify many streams in petroleum refineries, petrochemical plants, natural gas production plants, and chemical plants. In refineries, zeolite adsorbents remove impurities detrimental to downstream processing, including catalyst poisons (e.g., oxygenates and sulfur), corrosive agents, and chloride compound byproducts from processes using chloride catalyst promoters (e.g., catalytic reformers).

In natural gas production, zeolite adsorbents are used to dry the gas to prevent freezing and corrosion in pipelines, to remove sulfur compounds from the gas or LPG fractions to prevent corrosion in burners, and to remove compounds that are obnoxious or toxic (such as the odoriferous hydrogen sulfide and mercaptans in natural gas that form sulfur dioxide pollutants when burned for home cooking and heating). Worldwide, >1,000 units process tens of billions of cubic feet of natural gas daily.

Zeolites are used in the preparation of very high-purity fluids for special uses: e.g., gases used in the manufacture of electronics or gases and liquids used in modern analytical laboratory instruments.

Air Separation by Pressure Swing Adsorption (PSA) Processes.

The following draws primarily from reviews (47–52) plus the author's personal reflections from direct involvement in zeolite adsorbent development over the last 30 years. Many zeolites adsorb N₂ more strongly than O₂ [the possible use of zeolites in air separation was indeed the principal impetus for the pioneering work of Milton (11)]. Also, because zeolites adsorb more of both N₂ and O₂ from air with increasing pressure, air can be separated by using a PSA process. The air is passed at an elevated pressure through a bed of zeolite particles that adsorb the N₂ more strongly and hold it on the bed but allow O₂ to pass through the bed. Then, the adsorbed N₂ is discharged from the feed end of the bed as the pressure in the bed is lowered. Many variations on the process cycle were developed to improve efficiency and capital and operating costs.

The PSA and vacuum-swing adsorption (VSA) processes use zeolite adsorbents to produce O₂ of 90–94% purity (the balance is primarily argon). The O₂ is used, for example, in the manufacture of steel, glass, pulp, paper (in delignification and bleaching), and chemicals and in nonferrous metal recovery, waste incineration, and bioremediation. Zeolites provide benefits in energy efficiency, process efficiency, improved processing rates and product quality, and environmental impact.

Over the last 25 years, improvements in the PSA and VSA O₂ processes were driven by the development of zeolite adsorbents with improved N₂ capacity and selectivity. Zeolites such as NaX and CaA made possible the development of the first economical PSA O₂ process at a relatively small scale [up to ≈15 U.S. tons of O₂ per day (tpd)] in the early- to mid-1970s. Zeolite adsorbents, such as CaX (53), and third-generation adsorbents, such as LiX (54), LiC (55, 56), and MgA (57),

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together with improved (vacuum PSA or VSA) processes have dramatically reduced both capital and operating costs. Of the third-generation Type X zeolites, only LiX has been used commercially as of 1997.**

From the mid-1980s to the mid-1990s, these improvements provided a 5-fold reduction in adsorbent inventory and a nearly 2-fold reduction in power requirements. The commercial viability of a simple two-bed VSA system expanded to well over 100 tpd, and that of an even simpler one-bed system expanded to well over 40 tpd, allowing use of these noncryogenic systems in many applications formerly served by the cryogenic distillation of air. For the delivery of O₂ of 90–94% purity, single-bed units are more economical because of lower capital costs (although with higher energy costs) than liquid O₂ delivery in the 4–57 tpd range. Two-bed units have lower energy costs (but higher capital costs) and are more economical than either liquid O₂ delivery or on-site cryogenic plants in the 57–235 tpd range.†† In 1994, VSA plus PSA O₂ production was estimated to be 4–4.5% of the world demand for O₂, the fourth largest chemical at 39 billion pounds in 1995 (51). In 1996, PSA/VSA O₂ production was estimated to be >3,500 tpd in the USA and >10,000 tpd (>265,000 Nm³O₂ per hour) worldwide (47). Assuming a value of \$20 per ton of O₂, this production corresponds to a total market value of more than \$75 million per year, and growing.

Manufacturing Industries and Consumer Products Applications

Small Oxygen Concentrators for Medical Use (Medox).

In the U.S., a dozen companies manufacture small-scale PSA oxygen concentrators for patients with emphysema and chronic obstructive pulmonary disease. As with the large-scale PSA O₂ units, these small PSA concentrators use zeolites to produce 90 and 95% pure oxygen, the balance mainly argon and nitrogen. They can dramatically improve the quality of life.

The PSA units are engineered to be small (about the size of a small end table), readily transportable, (weighing ≈40 pounds), quiet, and reliable. They use 3–7 pounds of zeolite adsorbent to produce between 3 and 6 liters per minute of oxygen. Users are freed from needing high-pressure cylinders of PDF oxygen delivered or stored in their homes. Use of these concentrators has grown substantially over the Help last 20 years (S. R. Dunne, personal communication). In 1996, home medical equipment reimbursements (from U.S. Medicare) associated with oxygen concentrators totaled \$1.1 billion (58). Most are PSA units, the rest being primarily membrane units, which produce much lower oxygen concentration.

Automotive Air-Conditioning and Stationary Refrigerant Drying.

Zeolite desiccants remove water and acids formed by breakdown of the refrigerant mixed fluid thus protecting the system from freeze-up and corrosion. UOP supplied zeolite 4AXH-5 desiccant for automotive use and 4A-XH-6 for stationary refrigerant drying. These desiccants dominated the refrigerant

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industry for use with refrigerants R-12 and R-22 and the associated mineral oil lubricants. However, the 1987 Montreal Protocol heralded their demise because the very long life of fugitive R-12 emissions in the atmosphere became linked to ozone depletion and global warming.

The leading contender to replace R-12 was R-134a refrigerant, but R-134a was found to be unstable in the presence of the 4AXH-5 desiccant, leading to acids, sludge, deterioration of the desiccant, and possible failure of the refrigerant system. A UOP team developed the new XH7 zeolite desiccant, which is compatible with the new R134a lubricant systems, to meet the critical legislated deadlines. The deadlines for original automotive equipment manufacture and fleet testing were set at 3 years before system production, an extremely short development time for such a complex application.

Another new zeolite desiccant, XH9, was developed a couple of years later; in addition to automobiles, it is widely used in refrigerators (home refrigerators, supermarket freezers, and display cases) and stationary air conditioners. Because XH7 and XH9 desiccants are also compatible with systems using R12 refrigerant and mineral oil lubricants, dryers using the new desiccants can be prefit into R12 systems before total conversion to R134a systems. The XH7 desiccant today holds almost all of the automotive air-conditioning market formerly held by the 4AXH-5 desiccant before the advent of the new refrigerants. Consumers benefited because the availability of current systems was not disrupted and any danger to the environment was alleviated: hence, the American Chemical Society Heroes of Chemistry Award in March 1998 to the UOP team (A. P. Cohen, S. L. Correll, P. K. Coughlin, and J. E. Hurst).

Worldwide, millions of pounds of zeolite desiccants are installed in air conditioning units in passenger cars and light trucks. For stationary systems, most refrigerators in the U.S. and many elsewhere use zeolite desiccants to dry and remove acids from the refrigerants. The new desiccants, together with hermetically sealed systems with internal pumps, have extended the service life of refrigeration units by at least two to three times.

Air Brake Dryers for Heavy Trucks and Locomotives.

Most goods produced worldwide are moved to market by heavy trucks and locomotives whose brake systems are actuated mostly by clean dry air at high pressure. Air brake systems are engineered to be fail-safe: When the air supply system fails, the brakes engage and prevent the trucks or locomotives from moving.

A key element of the air supply systems of a truck is a PSA dryer, typically using a single packed bed of ≈ 3 pounds of molecular sieve to dry the compressed gas; locomotives require more absorbent. The air compressor on a truck runs for 1–3 min at a time. The compressed gas is dried and passed to a reservoir that in turn supplies air pressure to the brakes to prevent the unintended actuation of the brakes while the truck is moving. When the reservoir is full, a signal shuts off the compressor; the dryer is depressurized, and a little dry air is bled back through the dryer to partially regenerate the bed of molecular sieve (S. R. Dunne, personal communication). These dryers have significantly improved the reliability and safety of braking systems for large trucks and locomotives.

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Insulated Glass Windows.

Most insulated glass produced worldwide is manufactured with desiccant contained in channels (or in matrices) that separate the panes of double-, triple-, or quadruple-paned windows. The desiccant scavenges moisture and other trace compounds, such as solvents or plasticizers, that may evolve during manufacturing. Although the sealants used for the manufacture of insulated glass windows are excellent, a finite amount of moisture still leaks into the windows over time. Desiccants, primarily zeolites, prevent fogging, mists, or formation of dew between the windowpanes because they lower the dew point of the gases inside the windows to levels far below the lowest expected surface temperature of the glass. Insulated glass provides aesthetic features, improved human comfort, and energy savings that make them a truly economical and beneficial addition to both commercial buildings and homes (S. R. Dunne, personal communication). Residential and nonresidential dual-pane (insulating) windows and patio doors containing zeolite adsorbents have a total window area of ≈ 46 billion square feet worldwide. The estimated present energy savings in heating during winter and cooling during summer from the use of these insulating windows is equivalent to 450 million barrels of oil per year.

Environmental Protection Applications

In addition to the benefits already listed, many other applications provide environmental benefits.

Builders for Phosphate-Free Laundry Detergents.

In the 1960s, growing public awareness of eutrophication of natural waters led to efforts to reduce the inflow of plant nutrients, especially phosphate and ammonia or nitrate. Dead algae sinks to the bottom of a pond or lake, where it depletes the oxygen in the water. Too much growth of algae depletes oxygen so much that fish die. As a result, many states, particularly those bordering the Great Lakes, banned phosphate in laundry detergents.

The prime function of phosphate “builders” in laundry detergent powders is removal of the hardness ions Ca^{2+} and Mg^{2+} in the wash water by complexing. Zeolite ion exchangers in powder form also can provide this service by removing Ca^{2+} and Mg^{2+} ions from the solution and replacing them with soft ions such as Na^+ . Zeolite NaA was known to have high selectivity and capacity for calcium, and its application as a builder in heavy-duty powder detergents was developed in the 1970s, primarily by scientists at Henkel (59, 60, 61) in Germany and Procter and Gamble (61, 62) in the U.S. Round NaA zeolite particles, a few micrometers across, are small enough to pass through the openings in the weave of the fibers in clothing and are not filtered out to form encrustations on the cloth. Recently, zeolite P (GIS), as maximum aluminum P or MAP, was developed by scientists at Unilever (and Crossfield) (63) as an alternative builder for the same applications, and debate on the relative merits of NaA and NaP zeolites continues (64). Today, the conversion of the USA detergent market to zero-phosphate formulas is virtually complete. In Europe, one-third of the powder detergents are zeolite based, and Canada is $\approx 50\%$ converted. Latin America and many of the Pacific region countries are converting to zero-phosphates (65).

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In 1987, the Kao Corporation in Japan introduced Attack, a compact powder detergent that has higher bulk density and higher surfactant level and needs lower dosage. Use of compact powders in the Japanese laundry market grew to >90%. In the U.S., from 1990 to 1994, the use of compact powders grew from 2% to >90%. All compact powders in the U.S., Europe, and Japan have no phosphates. Zeolites used as builders in compact powders serve as particle-formation aids. This use of zeolites has facilitated changes in the process of detergent manufacture from spray drying and to alternative processes such as agglomeration. This shift, in turn, has led to increased use of zeolites in laundry detergent powders.

Automotive Emissions Control.

New stable zeolites have been used successfully in diverse automotive emissions control problems. A very serious challenge in automotive emissions control today is control of nitrogen oxides (NO_x) emitted from lean-burn diesel engines. Many catalyst developers and academic researchers are using zeolites with a wide array of added base and precious metals as catalysts to enable hydrocarbon storage, NO_x reduction, and oxidation of both hydrocarbons and CO. Today, zeolites are used commercially for enhanced hydrocarbon oxidation in conventional diesel engines and NO_x reduction. Four-way catalysts, which provide NO_x reduction, HC oxidation, CO oxidation, and particulate control, are being developed.

For gasoline-fueled vehicles, the most-serious problem is the cold-start period. Over 90% of the hydrocarbon emission by a car during a cold start occurs within the first 3 min of engine operation. A hydrocarbon trap must contain an adsorbent that captures most of the hydrocarbons during this period. Once captured, most of the hydrocarbons must be held by the adsorber until the catalytic converter has heated up enough to be capable of oxidizing them. Then the adsorber must release the hydrocarbons to be oxidized, rendering them harmless to the atmosphere.

The adsorber also must be mechanically, thermally, and hydrothermally durable enough to withstand the harsh environment of the exhaust gas stream. Especially since 1995, major advances have been achieved in the development of hydrocarbon traps. Improved hydrothermal stability of the molecular sieve adsorbent, improved chemistry of the wash coating, and the addition of a noble metal catalyst directly onto the adsorber brick are technical milestones that enable successful implementation of hydrocarbon traps in emissions control (S. R. Dunne, personal communication).

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Several major automakers have demonstrated excellent emissions reduction and system durability. General Motors achieved 50,000-mile-aged converter performance that surpasses Environmental Protection Agency requirements for use on a car designated as a low-emissions vehicle: i.e., a vehicle must emit nonmethane hydrocarbons at a weighted rate <0.075 grams per mile in the U.S. federally mandated test protocol. Mercedes Benz has achieved emissions that beat the ultralow-emissions vehicle standards of <0.04 grams per mile in the same testing (S. R. Dunne, personal communication).

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The total U.S. car and light truck production rate is ≈ 12 million vehicles per year. Over the next 10 years, emissions control technologies of all kinds will be implemented to keep the auto manufacturers in compliance with the law. Europe has a larger vehicle production rate and more eligible vehicles.

Radioactive Waste Management.

A special use category that is small in both the quantity of both molecular sieves and the gases and liquids processed is radioactive waste management, in which zeolites and other new molecular sieve ion exchangers (**66**, **67**), adsorbents, and catalysts have been used for >25 years. Although only small quantities are used, the past and future environmental benefits are large indeed.

UOP's IONSIV zeolite ion exchangers were used for the radioactive waste cleanup at Three Mile Island; the West Valley commercial nuclear fuel reprocessing site; and the Hanford, Savannah River, Oak Ridge, and other U.S. Department of Energy nuclear waste storage sites (**67**). Most recently, and of special interest, is the current use of the new IONSIV IE-911 crystalline silicotitanate (CST) ion exchangers for the cleanup of the radioactive wastes in the Melton Valley tanks at Oak Ridge (**68**) and the planned use elsewhere in similar and other applications. The effectiveness of CST was discovered (**69**) by researchers at Sandia National Laboratories and Texas A & M University, and its further product and manufacturing process development and commercial manufacture was carried out in 1994–1995 by UOP under a Cooperative Research and Development Agreement with Sandia (**70**, **71**). In 1996, this work earned an R&D 100 Award for the Sandia, Texas A & M, and UOP researchers (**72**).

Other Smaller Environmental Applications.

Many smaller applications of zeolites in catalysis and adsorption, although important and beneficial to mankind, are not discussed here because of space limitations. Noteworthy are the growing uses of zeolites and other molecular sieves as adsorbents in separations of volatile organic compounds and other pollutants, in desiccant cooling and dehumidification, and as ion exchangers for pollution abatement and toxic waste management.

Conclusions

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Likely Future Applications.

Use of zeolites as catalysts in the manufacture of some fine chemicals should expand. New zeolite and other microporous oxide catalysts should be developed with improved selectivity and new functionalities, perhaps for strong base and oxidation catalysis, chiral synthesis, and possibly, membrane reactors. Desiccant cooling and dehumidification, and sorption heat pumps, may achieve serious success. New ion exchange applications of new microporous oxides also may be expected. Experience has taught that the availability of new materials normally precedes by many years the discovery of all of their useful properties and the conception and development of new uses.

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Impacts of Molecular Sieves on Human Welfare.

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From these numbers, Roth estimated the value of fuels and chemicals produced using catalysts in 1989 to be \$891 billion per year, or 17% of the U.S. gross national product, and judged the corresponding worldwide product values for fuels and chemicals to be \$2.4 trillion per year (**73**). Of course, not all catalysts are based on zeolites, but for petroleum-based fuels and petrochemicals, most catalysts are now zeolitic. Thus, the impact of zeolites in these areas is clearly great. Likewise, the use of zeolites in catalytic converters to reduce undesirable emissions from vehicles also represents a significant present market (with large growth potential) and substantial benefits to mankind in pollution abatement.

As described earlier, synthetic zeolites play critical roles in the production of fuels, petrochemicals, and other products essential to modern societies; in pollution avoidance or abatement; in energy efficiency; and in the efficient use of natural raw materials. They also contribute to the quality and performance of the ultimate products because of the greater purity and uniformity of the intermediates made by using zeolites.

The many benefits achieved from the applications of zeolites and other molecular sieves are the fruits of the basic investments made decades ago, and into the present, in the research areas of mineralogy, geology, geochemistry, structure and properties of natural zeolites, exploratory materials synthesis, materials characterization methods and their application, and exploratory research on structure, property, and functionalities. The basic concepts and understanding from these efforts, coupled with creative consideration of how the properties and functionalities so discovered might be of service to solve the needs of mankind, continue to create new benefits.

Acknowledgments

We all contribute by standing on the shoulders of giants. In the field of synthetic zeolites and related materials, and their applications, my personal giants include R. M. Barrer, R. M. Milton, D. W. Breck, E. M. Flanigen, J. A. Rabo, L. B. Sand, P. E. Pickert, C. G. Gerhold, D. B. Broughton, G. T. Kerr, G. H. Kuehl, J. J. Collins, G. E. Keller, W. M. Meier, and J. V. Smith. In various ways, the prior work of each has had specific impact on my own work over the years. I also gratefully acknowledge the contributions of my many friends and colleagues at UOP, especially P. T. Barger, J. C. Bricker, A. P. Cohen, N. A. Cushner, R. Dunne, G. J. Gajda, S. H. Hobbs, J. A. Johnson, D. C. Kaminsky, P. J. Kuchar, R. L. Patton, M. W. Schoonover, B. V. Vora, S. T. Wilson, and C. M. Yon, the thoughtful secretarial support of Sharon Lambert, and the skilful editorial support of Sandy Weiss. I thank J. V. Smith and the National Academy of Science for organizing this colloquium and inviting this contribution and thank UOP for supporting this endeavor and many others. Finally, I thank my wife, Carol, for patience and understanding.

Footnotes

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↵* The three-letter International Zeolite Association Structure Commission code for the framework topology of each zeolite is given in parentheses at the first mention of that zeolite in this paper (the full list is at <http://www-iza-sc.csb.yale.edu/IZA-SC/>).

↵† The molecular sieves of AlPO₄s, SAPOs, MeAPOs, etc., were discovered in the 1980s by scientists in the Tarrytown, NY laboratories of Union Carbide Corporation's Catalysts, Adsorbents and Process Systems (CAPS) group. In 1988, Union Carbide Corporation's Catalysts, Adsorbents and Process Systems and the Process Division of UOP of AlliedSignal merged to form a partnership company, called UOP, which is jointly owned by AlliedSignal and Union Carbide. UOP LLC has continued to develop both the materials and their applications.

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SAPO,
silicoaluminophosphate;
8R,
eight-ring;
EB,
ethylbenzene;
PSA,
pressure swing adsorption;
VSA,
vacuum swing adsorption;
tpd,
U.S. tons of O₂ per day;
3D,
three-dimensional

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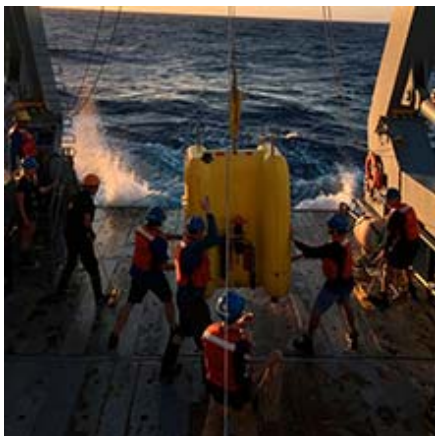
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